COMPUTATIONAL STUDIES OF THE RHEOLOGICAL

PROPERTIES OF ANISOTROPIC COLLOIDS

by

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ABSTRACT

Understanding the rheology of colloidal suspensions is of significant importance for both fundamental interest and practical applications. Many industrial processes and products rely on either the stability of colloidal suspensions, such as in the foods, adhesives and paints, or the aggregation of colloids out of suspension, such as for optical crystals. These processes and products will inevitably experience external forces and understanding how the colloidal suspensions will react to these external forces is very important to industry.

It is well established that the microstructure plays a key role in the rheological behaviour of colloidal systems. The focus of colloid rheology has largely been on suspensions of spherical colloidal particles, where the inter-particle interactions, which govern the microstructure, are isotropic. It would be of fundamental interest to study systems that are able to produce more complex microstructure, and therefore potentially interesting rheological behaviours. Since the turn of the 21st century, advances in particle synthesis have made available a variety of colloidal particles that involve anisotropic inter-particle interactions due to shape and/or surface chemistry. Colloidal dumbbells offer an attractive model system to advance our understanding of how the microstructure governs colloidal rheology beyond the well-studied isotropic limit. In this context, we have investigated systems of symmetric as well as asymmetric colloidal dumbbells, interacting via depletion interaction, using Brownian Dynamics simulations.

We find that for dense suspensions of symmetric colloidal dumbbells interacting via depletion, the aspect ratio, i.e. the length-to-breadth ratio, critically influences the shear viscosity of the suspensions, which exhibit a non-monotonic variation with the aspect ratio showing a minimum at an intermediate value. This non-monotonic behaviour becomes more pronounced as the effective packing fraction increases. We argue that the non-monotonic variation of the shear viscosity with the aspect ratio is a manifestation of translation-rotation decoupling. The suspension exhibits shear-thinning behaviour, which we attribute to a microstructure arising from an alignment of the axis of the cylindrical symmetry with the flow direction.

For asymmetric colloidal dumbbells, we exploit the size ratio and a hierarchy of interactions between the lobes to promote self-limiting cluster formation upon gradual cooling. The cluster fluid becomes more viscous as the fraction of colloidal particles forming tetramers grows upon cooling. Under an external shear, we observe a strong shear thinning behaviour, which is attributed to the disassembly of the clusters with increasing shear rate. This study found that the shape and surface chemistry can be exploited to form clusters in a controlled way to manipulate colloid rheology.

When the system of colloidal symmetric dumbbells is subject to a temperature quench, the arrested structure is found to show local ordering that is sensitive to the aspect ratio. At a lower aspect ratio, the system undergoes shear-induced crystallisation into a close-packed structure, whereas at a high aspect ratio the system arrests into a gel-like structure.

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1. INTRODUCTION

1.1. Colloidal suspensions

Colloids are systems with particles in one phase dispersed in a continuous phase made of constituents on a much smaller length scale [1]. A variety of colloidal systems exist, depending upon whether the disperse and continuous phases are solids, liquids or gases. Examples of this are emulsions such as milk, where a liquid is dispersed within a continuous liquid phase; or gels, where a liquid is dispersed within a solid phase. In the terminology of sol-gel transition, when solid particles dispersed in a liquid medium form a space spanning network, one obtains a *colloidal* gel that ceases to flow and supports yield stress. In this thesis, we focus on colloidal suspensions, where solid colloidal particles are dispersed in a liquid phase. The size of the colloidal particles ranges roughly from 1 nm to 1 μ m.



Figure 1: Image reproduced from Ref 2. An example of colloids imaged using confocal microscopy. On the left is a hexagonal close packed colloidal crystal layer of PMMA particles. On the right is an image of the same particles in fluid suspension.

Colloidal suspensions are of wide interest because of both fundamental and practical reasons. It has been suggested by Poon [3] that "colloids made up of relatively large

particles can behave in the same way as much smaller counterparts in the molecular world; for some purposes, colloids behave as "big atoms". This is one reason why colloid science has been of such interest. Colloids can act like atoms, but have properties that enable experiments, which cannot be done with atomic or molecular systems [4]. For example, due to the size of colloidal particles, colloidal particles move on a much longer time scale (seconds) than their molecular counterparts. As a result, the pathways for crystallisation, and other interesting phase transitions, are much easier to study with colloidal particles than in molecular systems. The size of colloids also make them easily observed using optical microscopy [2], and are especially conducive for many applications such as encapsulation and photonic materials.

There is great interest in the kinetic stability of this type of colloidal suspension in the consumer goods industry. An increased kinetic stability can lead to longer shelf life of a product, or a more robust product that can withstand transport and storage in different conditions. This applies to a wide variety of goods in industry, including food, cleanliness products, adhesives, paints etc. [5, 6].

Another interesting property of the system is to overcome the kinetic stability and bring the colloids out of the continuous phase. The aggregation of the colloids can have many applications including optical crystals, drug delivery systems and oil recovery [7–9]. Optical crystals utilise the controlled formation of colloids into crystal structures to propagate light, whereas drug delivery and oil recovery both utilise the controlled aggregation of colloids around a desired product to transport it to a target location before release.

With such sought after applications in industry, the comprehensive study of colloid suspensions is of great importance. These products and applications would experience external forces during transport, storage and use, therefore, how the system reacts to an external force is also vital to industry.

1.2. Colloidal interactions

One of the attractive features of colloidal suspensions is that the interactions between the suspended colloidal particles are tunable. Understanding colloidal interactions is critical to controlling the stability of colloidal suspensions. Colloidal interactions can be manipulated to engineer the phase behaviour of colloidal suspensions [10], and also their rheological properties [11]. The microstructure of colloidal suspensions, i.e. the spatial distributions of the colloidal particles in suspensions, are influenced by the forces at play.

The ubiquitous presence of attractive van der Waals forces require colloidal suspensions to be stabilised by invoking repulsive interactions. The London dispersion forces, due to instantaneously induced dipoles in non-polar particles causing fluctuating attractive forces, account for the ubiquitous presence of the van der Waals forces. In the case of charge-stabilised suspensions, the surface of the colloidal particles acquires charges due to the ionisation of the surface groups; the counterions dispersed in the medium satisfy the electro-neutrality condition. The charge distribution around a colloidal particle in the medium forms what is known as an electric double layer. Some of the counterions are bound to the surface forming the Stern layer, with a diffuse layer carrying an excess of charges of the same sign as the counterions, in close proximity to the surface but under thermal motion. When the colloidal particles come close together, the double layers around each particle start to interact, giving rise to a screened electrostatic repulsion. The effective screened electrostatic repulsion between a pair of spherical colloidal particles, derived by Boris Derjaguin and Lev Landau [12], and independently by Evert Verwey and Theodoor Overbeek [13], is given by

$$U_{\text{repulsion}}(r) = \left[\frac{Q \exp(\kappa R)}{1 + \kappa R}\right]^2 \frac{\exp(-\kappa r)}{4\pi\epsilon r}$$
(1)

where Q is the charge of the colloidal particles, ϵ is the vacuum permittivity, R is the radius of the spherical particles and r is the distance between the centres of the particles. Here, κ is the inverse Debye screening length, which controls the range of the screened electrostatic repulsion, in the limit of the Debye-Hückel approximation.

The interplay between the attractive van der Waals forces and the repulsive electrostatic forces is what governs the stability of the colloidal suspension. One of the earliest theories to explain this interplay in the interparticle interactions between colloidal particles is the DLVO theory, named after the four authors who derived the expression for the electrostatic force [12, 13]. The model potential derived from the DLVO theory, called the DLVO potential, is given as

$$U_{\rm DLVO}(r) = \left[\frac{Q \exp(\kappa R)}{1 + \kappa R}\right]^2 \frac{\exp(-\kappa r)}{4\pi\epsilon r} - \frac{A_{\rm H}}{12} \left[\frac{4R^2}{r^2 - 4R^2} + \frac{4R^2}{r^2} + 2\ln\left(\frac{r^2 - 4R^2}{r^2}\right)\right]$$
(2)

The second term in the above expression is due to the attractive van der Waals interaction, where $A_{\rm H}$ is the Hamaker constant. Figure 2 shows the distance dependence of the DLVO potential in a solid line, with the contributions from the repulsive and attractive components separately in dashed lines. First, a potential minimum is present due to the strength of the van der Waals force at very short distances between the two particle centres. As the two particles move further apart, we observe a maximum that arises from the dominating electrostatic repulsion as the van der Waals forces weaken. Often, at even further centre-to-centre distances, a secondary minimum is observed as the electrostatic repulsion is generally short-ranged resulting in the van der Waals forces becoming dominant once again. Eventually the two forces become negligible meaning there is no interactions between the two particles, culminating in a potential energy of zero. The height of the maximum indicates the stability of the colloidal suspension as the thermal energy must be greater than the energy barrier, created by the maximum, for aggregation of the colloidal particles to occur.



Figure 2: The DLVO potential as a function of the distance between two spherical colloidal particles, r. The total potential energy (solid line) is derived from the contributions from the screened electrostatic repulsion and attractive van der Waals interactions (dashed lines).

Beyond the simple charge-stabilised colloidal interactions, there are a multitude of ways of introducing additional tunable forces to the colloidal system. An example of an interaction introduced to stabilise the colloidal suspension is steric repulsion. Short polymers are adsorbed onto the surface of the colloidal particles denying two particles from getting close enough together for the van der Waals forces to overtake the electrostatic repulsion, therefore causing an effective repulsion.

As well as controlling the repulsion between colloidal particles, attractive forces can be introduced to these systems causing aggregation of the colloidal particles out of the continuous solvent phase. One such attractive force comes from the addition of non-adsorbing polymers to the colloidal suspension, which can be easily tuned to change the phase behaviour of the system.

At a sufficient concentration and size of non-adsorbing polymer, the colloidal suspension separates into a colloid-rich phase and colloid-poor phase [14]. Assuming the polymers are small, relative to the colloidal particles, an exclusion zone is created around the surface of the large colloidal particle. This exclusion zone is where the centre of mass of these polymers cannot penetrate, decreasing the entropy of the system due to the restriction to where the polymers can move.

The large colloidal particles in the system can approach each other causing their exclusion zones to overlap, resulting in a reduction of the total exclusion zone in the system, allowing the polymers more space to move freely. The increase in free space creates an increase in entropy, meaning the overlapping of exclusion zones is favourable to the system. This favourable interaction promotes the attraction of the colloidal particles in the system, pulling them out of suspension and leading to aggregation. This interaction has been called the "depletion flocculation" or "depletion attraction". The interaction has gone on to be integral in food stuffs, pharmaceuticals, paints and other industrial products. A simple graphical representation for this interaction is shown in Fig 3.



Figure 3: Image reproduced from Ref 3. Showing colloids in green, polymers in blue, the exclusion zone in grey and the overlap of exclusion zones in red.

Early observations of this attractive interaction were first documented by Asakura and Oosawa [14], with the early model named after them, the Asakura-Oosawa Model. The interaction was also independently documented by Vrij [15]. The colloidal particles are modelled as hard spheres of diameter σ_C and the polymers as soft spheres with the diameter derived from the radius of gyration, $\sigma_P = 2R_g$.

$$U_{CC}(r_{ij}) = \begin{cases} \infty, \text{ if } r_{ij} < \sigma_C \\ 0, \text{ if } r_{ij} > \sigma_C \end{cases}$$
(3)

$$U_{CP}(r_{ij}) = \begin{cases} \infty, \text{ if } r_{ij} < (\sigma_C + \sigma_P)/2 \\ 0, \text{ if } r_{ij} > (\sigma_C + \sigma_P)/2 \end{cases}$$

$$\tag{4}$$

With the colloidal particles being hard spheres, the colloid-colloid potential, $U_{CC}(r_{ij})$, and

colloid-polymer potential, $U_{CP}(r_{ij})$, are simple repulsive potentials with infinite repulsion at the point of surface-to-surface contact. There is no potential energy when the particles are not touching. The polymers in the Asakura-Oosawa model are soft spheres, allowing them to pass freely through each other.

In this early model, only the entropy of the system through packing made an impact on the phase behaviour observed for the colloid-polymer mixture. It was seen later that the polymers can be integrated out from the model to produce an effective potential between the colloids [16]. With a large enough difference in the size ratio between the colloids and polymers in a mixture [17], the colloid-colloid interaction can be described by

$$\frac{1}{k_B T} U_{eff}(r) = -\frac{\pi}{6} \sigma_P \zeta_P \left(1 + \frac{\sigma_C}{\sigma_P}\right)^3 \left[1 - \frac{3r}{1 + \sigma_P} + \frac{2r^3}{2(1 + \sigma_P)^3}\right], \sigma_c < r < \sigma_c + \sigma_P$$

$$(5)$$

where ζ_P is the fugacity which governs the control of the concentration of the polymers in the solution, given by

$$\zeta_P = \Lambda_P^{-3} exp\left(\frac{\mu_P}{k_B T}\right) \tag{6}$$

where Λ_P^{-3} is the de Broglie wavelength and μ_P the chemical potential of the polymers.

Following the hard sphere colloid prescription of the early model, the effective colloidcolloid potential goes to infinity in the $r < \sigma_C$ regime and is zero in the $r > \sigma_C + \sigma_P$ regime. Although the Asakura-Oosawa model, including the effective potential, is a decent approximation of the depletion attraction seen in the hard sphere colloid-polymer system, the discontinuous nature of the model makes it a bad approximation for the vast majority of real colloidal systems. A continuous, empirical potential is better suited for our purposes.

Alongside the Asakura-Oosawa model, which provides a widely used theoretical description of the effective potential due to depletion, the Morse potential and generalised Lennard-Jones potential have also been used to provide an empirical description of depletion or more generally short-ranged attraction [18, 19]. For the body of the work presented in this thesis, dumbbell-shaped colloidal particles are represented using two sites held in a rigid framework and we used the generalised Lennard-Jones (GLJ) potential to describe the effective interaction between the sites. The GLJ potential will be described in detail in chapter 2.

The depletion attraction can be tuned via the size and concentration of non-adsorbing polymers in the system [20]. The size of the polymer is not always directly linked to the polymer chain-length but often described by the effective radius of the polymer, called the radius of gyration. The radius of gyration of a polymer, R_g , is defined as the root mean square of the distance of every monomer in the chain coil from the polymer's centre of mass.

The centre of the polymer, according to its radius of gyration, cannot penetrate the exclusion zones and so a larger radius of gyration means there would be a larger exclusion zone around the colloidal particles. A greater area of exclusion translates to a larger range in which the exclusion zones of two colloidal particles would overlap. Therefore, a larger radius of gyration would result in a larger range for the attractive interactions between the colloidal particles in the system to occur.

The concentration of polymers in the system would increase the strength of the attractive interactions between colloidal particles. With a larger number of polymers, the gain of free space when the exclusion zones overlap would affect more polymers and, therefore, it is ever more favourable for the colloidal particles to come together. In essence, an increase in concentration of non-adsorbing polymers would result in an increase in the strength of the attractive interactions between the colloidal particles in the system.

1.3. Colloid rheology

1.3.1. Hard sphere colloids

Rheology is the study of the flow of matter, or how matter deforms when forces are applied to them. An ideal liquid is purely viscous and an ideal solid is purely elastic [11]. By measuring the stress and strain experienced by materials, it is possible to quantify the viscosity (for liquids) and elastic moduli (for solids). However, a soft material is rarely ideal on either end of the spectrum. Soft matter exhibits both viscous and elastic properties, making them viscoelastic materials. Colloidal suspensions, as prototypical soft matter, can exhibit rich viscoelastic behaviour when an external force is applied to them.

It is well documented that the microstructure of the colloidal system affects the rheology [21–25]. However, it is still not completely understood exactly how the microstructure affects the rheology. Thus, it is vital to understand the microstructure of the systems we study and how the microstructure changes with different system parameters as well as under shear.

Colloidal suspensions, with their tunable interparticle interactions, exhibit rich phase behaviour and provide model systems to study the mechanisms of phase transitions [10]. A system of hard-sphere colloids, with no attractive interactions between the colloidal particles, exhibits one of the simplest phase diagrams. The phase diagram has a fluid phase and a crystal phase with a coexistence region [26], as shown in Figure 4. The region of coexistence has been of great interest in the field [26–28].



Figure 4: Phase diagram of a hard-sphere colloidal suspension, involving a fluid (F) phase and a crystal (C) phase and a region of coexistence of both fluid and crystal.

A key parameter in rheology is the viscosity of the system. In the spherical regime, Einstein [29] calculated the effective viscosity, η , of a system of hard spheres in dilute suspension. It was observed that the viscosity of the system increased linearly with the increase in volume fraction, ϕ , of the spheres. The relationship was given as

$$\eta = \eta_0 (1 + \frac{5}{2}\phi) \tag{7}$$

where η_0 is the viscosity of the solvent that the hard spheres are suspended in.

More than half a century later, Batchelor and Green [30] published a theory to determine the bulk stress of hard spheres in a semi-dilute suspension. From the bulk stress they calculated the viscosities and found a different relationship as a function of volume fraction compared to the dilute suspensions, given as

$$\eta = \eta_0 (1 + \frac{5}{2}\phi + 5.2\phi^2) \tag{8}$$

This relationship was calculated in the absence of Brownian motion. The random displacements felt by the hard spheres, due to the solvent when Brownian motion is taken into account, produce a slightly different relationship [31], given as

$$\eta = \eta_0 (1 + \frac{5}{2}\phi + 6.17\phi^2) \tag{9}$$

The rheology of hard-sphere colloid suspensions has been extensively studied [27, 28, 32]. Petekidis *et al.* [27] studied the behaviour at a volume fraction of colloidal particles near the region of coexistence. Specifically, their work focused on investigating colloidal glasses under stress. It is reported that these colloidal glasses in hard-sphere systems have a finite yield stress and recover elastically from applied shear [27].

When shear is applied, the viscosity of a Newtonian (pure) fluid is independent of the rate of shear. However, in a viscoelastic system, shear thickening and thinning behaviours can be observed; where the viscosity increases (dilatant fluid behaviour) or decreases (pseudoplastic behaviour), respectively, as increasing shear is applied, as seen in Figure 5. Often these non-Newtonian behaviours are observed when a yield stress is exceeded. Yield stress being an amount of stress needed to be exceeded for a irreversible change in microstructure, called plastic deformation, to occur.



Figure 5: Image reproduced from http://polymerdatabase.com/, accessed April 2018. shear rate dependence of viscosity in three systems. A Newtonian fluid, dilatant fluid (shear thickening behaviour) and a pseudoplastic (shear thinning behaviour).

The flow behaviour of colloidal suspensions is important for a variety of industrial applications. For example, in the concrete industry, if the concrete mixture is too shear thickening, the speed at which one can transport or apply the concrete will be limited to the point at which the concrete becomes too viscous to move efficiently. It is therefore of interest to monitoring and control the shear thickening behaviour for optimal performance.

Another example is ketchup and other bottled condiments, where the rheology of the product needs to be optimised. An optimal rheological behaviour allows only a small amount of shear stress to exceed the yield stress and cause shear thinning behaviour for the product to flow out of the vessel, but also ensures that the shear thinning behaviour is weak enough such that for the product does not become too runny and come out too fast. Effectively controlling shear thinning and thickening behaviour is clearly of much importance.

In recent work, Guy *et al.* [28] investigated the rheology of suspensions of hard-sphere particles as their size was varied. In particular, they were interested in the intermediate size regime of 1 μ m to 50 μ m, pushing past the colloidal size regime. It was shown that the transition from colloidal to granular flow in colloidal hard spheres was caused by shear thickening.

Wagner and Brady studied the shear thickening behaviour of colloidal suspensions [22], using Stokesian Dynamics simulations. According to this study, the system shows Newtonian behaviour at very low shear rates, shear thinning at intermediate shear rates and shear thickening at high shear rates.



Figure 6: Image reproduced from Ref 22, showing how the viscosity of the system changes as an increasing shear rate is applied. The hypothesis of microstructure relating to the behaviour is given in a cartoon representation.

The hypothesis that Wagner and Brady put forward is shown schematically in Figure 6. According to this hypothesis, the Newtonian behaviour is caused by an equilibrium microstructure, where the stochastic and interparticle forces are in balance with random collisions among particles that make the system resistant to flow [22]. When the shear rate is increased, the particles rearrange themselves into layers orthogonal to the sheargradient direction, making the flow easier and decreasing shear viscosity. However, at high shear rates, the hydrodynamic interactions between the particles become dominant over stochastic forces, leading to the formation of the so-called *hydroclusters*. Due to these transient density fluctuations, flow is hindered and a rise in shear viscosity is observed. This hypothesis was subsequently backed up by experimental imaging of the microstructure during shear by Cheng *et al.* [25]. However, more recently, a computational study by Xu *et al.* has suggested that the shear thinning behaviour is driven by structural changes at the pair level, as opposed to layering [23].

1.3.2. Attractive colloids

The addition of non-adsorbing polymers to a colloidal suspension can lead to phase behaviour of great complexity. An assortment of different phase behaviours can be observed depending on the relative sizes between the colloid and polymer, the concentration of each or even the starting conditions of the system [10]. For a set size of colloidal particle, large polymers show a phase diagram akin to an atomic system with an area of three-phase equilibria (gas + liquid + crystal) [33], whereas, small polymers show a phase diagram closer to a protein system with a metastable liquid-liquid area and two-phase coexistence. The concentration of polymer effectively represents inverse temperature. This can be seen in Figure 7, where the diagrams are inverted compared to phase diagrams of atomic and protein systems against temperature.

In 1992, Lekkerkerker et al. [33] employed a statistical mechanical model, which uses a



Figure 7: Image reproduced from Ref 10. Phase diagrams of one colloid size with large polymers on the left and small polymers on the right. The shade area on the left shows the region of three-phase equilibria.

van der Waals mean field-approximation, to calculate the phase behaviour and show the existence of the three-phase equilibria in systems with long-range attraction, i.e. large polymers. At the time, two-phase coexistence had been observed experimentally [34] but no work had shown the three-phase. Only around a decade later, Pusey *et al.* [4] and Calderon *et al.* [35] were able to independently observe the three-phase coexistence in experiment. Recently, Sabin *et al.* [36] also gave experimental evidence for the phenomena.

There are other unexpected phase behaviours that the colloid-polymer system can exhibit. For instance, in a recent study by Feng *et al.* [37], experimental and theoretical evidence was given for re-entrant solidification phase behaviour of a 2D system. For a readily used colloid-polymer system [38–40], the polymers were non-adsorbing at lower temperatures but actually became weakly adsorbing as the temperature of the system was increased. When the polymers are non-adsorbing the crystallisation via the depletion attraction was observed as expected. As the temperature was increased, the crystal melted, again, as expected. However, past a critical temperature, the polymers became weakly adsorbing and bridging between colloids observed flocculation of the colloids. The flocculation was reversible, which means if the system is cooled slowly, there is potential for using two different colloid materials and performing staged aggregation. The paper was limited to a 2D study but the researchers stated that the nature of the interactions, and therefore phase behaviour, are general so "could be readily applied to three dimension" [37].

A number of studies both experimental and theoretical have been conducted on the colloid-(non-adsorbing)polymer mixture, showing the presence of complex states such as the glassy state and the gel phases [41, 42]. Investigating the rheological properties of viscoelastic materials can give information on these microstructures formed, which can be very important for foods, like gel formations in yogurt-based foods [5], and other commercial products. Studying the effect of the parameters of a system on its rheological behaviour would be invaluable in designing novel soft materials for use in industry.

A number of experimental studies on the rheology of the colloid-polymer system have been undertaken [43–46]. Marzi *et al.* [43] studied a system opposite to the traditional colloid-polymer system, where small colloidal particles are added to large soft polymers. Rich behaviour is observed as the concentration of the small colloidal particles added is increased. At a high density of polymer, the addition of colloids cause the melting of a repulsive glassy state. Reentrant solidification is observed as the concentration of depletant is further increased, similar to that of the study by Feng *et al.* [37] With the polymer-induced depletion of the colloid suspension, a repulsive glass forms, melts and then the polymer becomes weakly-adsorbing to form an attractive glass microstructure. In the case of the polymer suspension, addition of the colloid depletant causes melting of the repulsive glass, and eventually the increase in total concentration counteracts the loss in repulsion and a repulsive glassy state is reformed. At sufficiently high concentrations of depletant, the strong attractive contribution eventually overcomes the repulsive glass to form an attractive glass. Marzi *et al.* [43] explain this reentrant behaviour in terms of an interplay between structural arrest and phase separation.

Another interesting rheological behaviour of the colloid-polymer system was studied by Harich *et al.* [44]. They found that as a gel formed from the polymer-induced depletion of a colloid suspension, dense "debris" gathered on top of the gel. If the debris was heavy enough, it would fall through the gel and cause a rapid gravitational collapse of the gel. They posit that identifying the origin of this debris would be key in fully understanding colloidal gels.

Extensive experimental work was done by Laurati *et al.* [46] on the colloid-polymer system at intermediate colloid volume fraction. By tuning the attractive interaction, they were able to locate the gelation boundary for the system. Using microscopic techniques, it was shown that the liquid phase, upon approaching the gelation boundary, started to cluster and form a space-spanning network [46]. Once the gelation boundary was crossed, a colloidal gel was formed. Laurati *et al.* [46] showed the data was consistent with modecoupling theory predictions of the rheology of the system. Unlike spherical particles, which have a shape such that every axis has the same dimensions, axisymmetric particles are symmetric in two dimensions with the third principle axis being different. The particles are commonly described using an aspect ratio parameter, L^* , that compares the length of particle along the principle axis with the dimensions of the particle in the other two axes. Axisymmetric particles cover a wide variety of shapes such as ellipsoids, rods, dumbbells etc. The anisotropy of these types of particles have been used as models for rod-like micro-organisms from as early as the 1940's by Onsager [47] and have continued to be studied in more recent research [48, 49]. The shape of these particles introduce shape anisotropy into the system, leading to novel behaviours moving away from the well studied spherical regime. The equilibrium phase behaviour shows many interesting phases appear due to the shape anisotropy of the axisymmetric particle.

Frenkel *et al.* [51] studied hard ellipsoid particles in simulation and observed the existence of plastic crystalline and nematic liquid crystalline phases. The phase behaviour seemed to be equivalent in both prolate and oblate ellipsoids. A decade later, a computational study of spherocylinders (elongated bodies similar to prolate ellipsoids) revealed a smectic-A liquid crystalline phase alongside the phases shown in the previous study [50]. The phase behaviour was studied more recently in experiment using confocal laser scanning microscopy with small angle X-ray scattering on colloidal silica rods, confirming the existence of the unique phases found in the computational studies and also revealing that both the smectic-B phase appears alongside the -A phase at high densities [52].



Figure 8: Image taken from Ref 50. This phase diagram of hard spherocylinders probes a range of densities against the elongation of the spherocylinder particles. There is the isotropic (I), plastic crystal (P), nematic (N) smectic (Sm) and closed packed solid (S) phases along with coexistence regions.

Under the presence of an external shear flow, suspensions of spherical colloidal particles generally exhibit a shear thinning behaviour with a sudden onset of shear thickening past a critical shear rate [22]. Leal and Hinch [53] demonstrated that even a small presence of shape anisotropy deviating from the spherical form can have a significant effect on the rheological behaviours of the system. From more than a century ago, it has been observed that elongated axisymmetric particles have complicated behaviours under shear flow compared to the spherical equivalent [54, 55]. Jeffery [55] solved the equations of motion for a small neutrally buoyant axisymmetric particle under a simple shear flow in the absence of fluid and particle inertia. Within those system conditions, Jeffery found that the particle rotates on infinite degenerate orbits coined "Jeffery orbits"; he speculated that the degeneracy would not last in a system with fluid and particle inertia and that the particle would settle on an orbit corresponding to the least energy dissipation. Soon

after the work was published, it was shown experimentally that an axisymmetric particle under shear flow adjusted through many Jeffery orbits until it eventually settled to a final optimum orbit of minimum energy dissipation [56]. A prolate particle would settle into a log-rolling orbit where the elongated principle axis of the particle is sitting perpendicular to the shear plane and the particle is rotating in the shear plane. An oblate particle would settle into a tumbling orbit where the flattened principle axis of the particle is sitting parallel to the shear plane and again the particle is rotating in the shear plane. Although these findings confirmed Jeffery's hypothesis that the particle would settle on the orbit corresponding to the least energy dissipation, it was observed much later both experimentally and theoretically that dumbbell shaped particles preferred to settle on the orbit of maximum energy dissipation, tumbling, when fluid inertia was present [57]. This work was focussed on suspensions in newtonian fluids however work has also been done on the dynamics of axisymmetric particles in non-newtonian fluids [58–60]. It has been observed numerically that a prolate particle suspended in a non-newtonian fluid settles on a log rolling orbit at weak shear flows and shifts to aligning in the flow direction and not rotate at higher shear rates [60].

The rheological behaviour of near-spherical spheroids have been studied by Leal and Hinch [53]. They focus their study on the effect of Brownian motion on the rheology of the spheroids and calculate the bulk stress of the system in a wide parameter space, varying aspect ratio and shear rate. In steady and oscillatory shear flow, they observed shear thinning behaviour that increases on increasing the rate of flow and/or frequency of oscillation. This work was soon accompanied by the extensive work of Brenner [61], who studied the rheology of dilute suspensions of rigid, axisymmetric particles. Again, this work observes shear thinning behaviour.

1.3.4. Colloidal dumbbells

Here we discuss the rheology and phase behaviour of a specific dumbbell-shaped axisymmetric particle as a particularly interesting system to study and the focal point for this thesis. A primary reason to focus study on a colloidal dumbbell particle system would be the relatively recent advances in the synthesis of the particle type. Several studies reveal simple techniques to fabricate dumbbell particles with varying lobe dimensions and surface chemistry in a controlled manner [62–65]. An important advance is in the formation of dumbbell particles in a mono-disperse manner which makes the transfer of observation between our one-component computational studies and experiment much easier. Chu et al. [64] demonstrated the mono-disperse synthesis of dumbbell-shaped microgels which are stabilised by electrostatic screening vis adding salt to the aqueous suspension, the mono-dispersity is shown in Figure 9.



Figure 9: Image taken from Ref 64. Demonstrating the mono-dispersity of the fabrication of polystyrene core, dumbbell-shaped microgels.

The shape anisotropy that the colloidal dumbbell particle introduces give rise to interesting microstructures. The phase behaviour of this system has been well studied using Monte Carlo simulations [66–68]. Dense suspensions of these particles transition into a plastic crystal regime in the near-spherical limit with an aspect ratio of less than 0.4, where an aspect ratio of 0 denotes a spherical particle. The nucleation process of the plastic crystal phase has been studied by Marechal and Dijkstra [68]. At higher aspect ratios, the plastic crystal phase is lost and instead we get direct transitions from fluid to closed packed regimes. An example of the phase diagram is given in Figure 10.



Figure 10: Image taken from Ref 68. There is the fluid, plastic crystal (PC) and the close packed (CP) phases along with coexistence regions. The diagram probes a range of reduced densities (ρ^*) and packing fractions (Φ) against how elongated the dumbbells are (L^*)

Heptner and Dzubiella [69, 70], studied colloidal dumbbells using Brownian dynamics, focusing their study on the near-spherical regime, at packing fractions that would produce the plastic crystal phase behaviour. The equilibrium study showed that the orientational diffusion of the particles is heavily affected by the increase in anisotropy of the dumbbells, i.e. the elongation [69]. Heptner *et al.* also studied the rheological behaviour of a symmetrical dumbbell system under oscillatory shear [70]. The phase transitions due to the external flow are similar to that of the hard sphere system, however the pathway is different. In the spherical system a shear-twinned FCC regime is observed at low strain, which transitions continuously to a regime of sliding HCP layers. In the dumbbell system this transition becomes discontinuous, with an intermediate disordered phase. Heptner *et al.* [70] attributes this difference in nature of the transitions to rotational-translational coupling and say this is a path that requires further study. It was also suggested that this coupling is the reason a sharp increase in the linear shear response above an aspect ratio of 0.15 is observed, despite the shape anisotropy of the system having little impact on the translational and rotational diffusion of the particles [69].

The rheological behaviour of soft dumbbells have been studied in the soft FENE (Finitely Extensible Nonlinear Elastic) dumbbell model and similar bead-spring models. Dlugogorski *et al.* [71] studied the FENE model and a generalised LJ model under steady shear and observed shear thinning behaviour much like the spherical system. The difference from the spherical system was that the onset of the shear thinning behaviour was delayed to higher shear rates in the dumbbell model. They suggested that the dumbbells behaved more elastically than the spherical system.

Sultan *et al.* [72] also used the FENE dumbbell model to study the rheology of polymers. They used FENE dumbbells in a standard DPD fluid to show that you can study macroscopic and mesoscopic scales simultaneously when using DPD. The study was mainly to prove the methodology but some rheological characteristics of the dumbbells were shown, in which they observed that the viscosity of the system decreased as the rigidity of the connecting rod was increased. The viscosity of the system increased when the maximum extension of the rod was increased. As a proof of their methodology they also showed, as known previously, that as you increase the polymer fraction (fraction of dumbbells) the onset of turbulence in the Couette flow was delayed to higher shear rates.

Townsend and Wilson [73] studied a bead-spring using two different spring models, Hooke's law and the FENE model. They tested this system using small and large amplitude oscillatory shear. Again, this study was mainly to test the applicability of their methodology of using Stokesian Dynamics to mimic the viscoelasticity of a polymer fluid. Much like in the work of Dlugogorski *et al.* [71], at large amplitude strain, the fluid showed shear thinning behaviour.

A couple of studies by Mandal and Khakhar [74, 75] have looked at the granular flow of inelastic dumbbell particles down a inclined plane with a rough surface both in two and three dimensions. Using this incline plane they studied both shear flow and chute flow, where chute flow includes gravity in the system. When looking at chute flow, they found that at the near-spherical limit the mean velocity of the dumbbells were slightly higher than for the spherical system due to the loss of symmetry and therefore local crystallisation. As the aspect ratio is increased further the mean velocity decreases greatly. When observing shear flow, they found the flow was homogeneous aside from wall effects and that increasing the aspect ratio resulted in an decrease in shear stress and pressure up to 1.4 (where 1 = sphere), beyond which they increased.

1.4. Thesis aim

In this context, the aim of this thesis was to investigate the rheological behaviour of suspensions of colloidal dumbbells interacting via depletion attractions, to understanding the effects of shape anisotropy on the rheological properties of the suspensions in connection with their microstructures so that the rheological behaviour can be controlled. To this end, we studied suspensions of symmetric as well as asymmetric colloidal dumbbells, using computer simulations. The objectives were as follows:

- 1. to investigate the effects of shape anisotropy on the rheological behaviour of suspensions of colloidal dumbbells and analyse the microstructures;
- 2. to establish design principles for self-limiting cluster formation to explore the effects on the rheological properties;
- 3. to explore routes to form colloidal gels in the presence of shape anisotropy.
2. METHODOLOGY

2.1. Model

We employed a one-component description that is traditionally used to model colloidal suspensions [76]. In this implicit-solvent representation, the solvent degrees of freedom are projected out and a pairwise additive effective potential is used to describe the interaction between colloidal particles. We considered colloidal dumbbells by treating them rigid bodies, each comprising two spherical lobes with interaction sites located at their centres. In our model, the effective potential between a pair of dumbbells is then given by the sum of site-site interactions, which, in turn, is described by the empirical generalised Lennard-Jones potential [19].

2.1.1. The generalised Lennard-Jones potential

The generalised Lennard-Jones potential between two spherical particles at a separation r_{ij} is given by

$$U_{\rm GLJ}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{2n} - \left(\frac{\sigma}{r_{ij}} \right)^n \right].$$
(10)

The widely used Lennard-Jones potential corresponds to (10) with n = 6. The potential has a repulsive term, corresponding to a softer core, and an attractive term. Here, ϵ is the depth of the well potential and represents the strength of the interaction, and σ is the distance between the two particle centres at which the potential is zero. Although the potential does not have a hard-sphere diameter, σ does provide an estimate of the diameter for the repulsive interaction to become dominant at distances less than σ . The exponent n controls the range of the potential. In our simulations, the length and energy are expressed in the units of σ and ϵ , respectively. The reduced units are discussed further in section 22.4.



Figure 11: The generalised Lennard-Jones potential for two values of the exponent: n = 6 and 24.

The Lennard-Jones potential is known to well describe the interactions between two inert gas atoms, and is extensively used in computer simulations of atomic and molecular systems. Figure 11 shows the generalised Lennard-Jones potential for two values of the exponent: n = 6 and n = 24. It is evident that the range of the potential becomes shorter as the exponent n increases with as shift in the distance at which the minimum occurs to a lower value. For n = 6, the potential is fairly long-ranged (approaching zero beyond 2.5σ with the minimum of the well at roughly 1.12σ), and therefore inadequate to describe the effective interaction between a pair of colloidal particles, which is short-ranged as compared to their diameters. In contrast, for n = 24, the potential has a much shorter range with the minimum occurring at roughly 1.04σ and the potential energy becoming nearly zero at 1.3σ .

In our studies, we opted to use the generalised Lennard-Jones potential, mostly with the exponent n = 24, to describe the effective interactions between colloidal particles when depletion attractions are at play. In case, any other exponent value was used, this will be explicitly mentioned.

2.1.2. Colloidal dumbbells

The colloidal dumbbells under consideration are represented as rigid bodies, each comprising two spherical lobes with interaction sites, which we label A and B, located at their centres. The site-site interaction is given by the generalised Lennard-Jones potential, so that the potential energy due to the interaction between two dumbbells is given by

$$U_{ij} = \sum_{a=A}^{B} \sum_{b=A}^{B} 4\epsilon_{ab} \left[\left(\frac{\sigma_{ab}}{r_{ab}} \right)^{2n} - \left(\frac{\sigma_{ab}}{r_{ab}} \right)^{n} \right]$$
(11)

where *n* is the generalised Lennard-Jones exponent, σ_{ab} and ϵ_{ab} are the Lennard-Jones parameters for the interaction between site a and site b belonging to dumbbell *i* and *j*, respectively, and r_{ab} is the corresponding site-site separation. The spherical lobes may differ in size and/or surface chemistry. In the case of symmetric dumbbells, any two interaction sites have identical Lennard-Jones parameters: $\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = \sigma$; $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB} = \epsilon$. We we used n = 24 for the range of interaction to be sufficiently short to describe depletion interaction.

It is important to note here that σ represents the pair separation at which the generalised

Lennard-Jones pair potential goes to zero. So, strictly speaking, σ does not represent the diameter of the spherical lobe. For a purely repulsive isotropic potential v(r), an effective diameter d can be given, following the prescription of Barker and Henderson [77], by

$$d = \int_0^\infty \left(1 - e^{-v(r)/k_{\rm B}T}\right) dr,\tag{12}$$

which yields the hard-sphere diameter for the hard-sphere potential. For the generalised Lennard-Jones potential with a relatively large value for the exponent n, the effective diameter is very close to σ . In the present study, the effective diameter d was taken to be σ as an approximation. For the symmetric dumbbells, the two spherical lobes have the same effective diameter, with their centres separated along the dumbbell axis by a distance L, as shown schematically in Figure 12. The aspect ratio of the dumbbell is denoted as L^* , and is defined by $L^* = L/\sigma$. $L^* = 1$ represents a dumbbell with two spherical lobes touching each other; for $0 < L^* < 1$, we have dumbbells where the spherical lobes are fused; the spherical limit is reached at $L^* = 0$. L^* thus provides a measure of shape anisotropy.



Figure 12: A symmetric colloidal dumbbell modelled as a rigid body, comprising two equal-size spherical lobes with the interaction sites located at their centres separated by a distance L. Here, σ is the Lennard-Jones length parameter, which is approximately equal to the effective diameter of each lobe.

The packing fraction for a colloidal suspension is the fraction of the volume that the colloidal particles themselves occupy while suspended in a liquid. In a one-component description with implicit solvent, the packing fraction is essentially the ratio of the volume that all the colloidal particles taken together occupy to the volume of the simulation box, i.e. $\phi = \frac{V_{\rm p}}{V}$. For a system of monodisperse spherical colloidal particles having diameter σ , the packing fraction is $\phi = \frac{\pi N}{6V}$. In the case of symmetric dumbbells, each comprising two spherical lobes of effective diameter σ , the packing fraction can be given by

$$\phi_{\alpha} = \frac{\pi N \alpha}{6V},\tag{13}$$

where α is a geometric factor, which takes into account any overlap as L^* varies between 0 and 1:

$$\alpha = 1 + \frac{3L^*}{2} - \frac{L^{*3}}{2} \tag{14}$$

For $L^* = 0$, $\alpha = 1$ recovering the spherical limit; $\alpha = 2$ when $L^* = 1$, corresponding two touching spheres of the same size.

For the asymmetric colloidal dumbbells that we considered, the two spherical lobes are only touching, but have different sizes and surface chemistry. We set $\sigma_{AA} = 1$ and $\epsilon_{AA} = 1$ with the length and the energy reduced by σ_{AA} and ϵ_{AA} , respectively. Our attempts to simulate a system of asymmetric dumbbells, where the second lobe has an effective diameter of $\sigma_{BB} < 1$, suffered from issues due to numerical instability while running the Brownian Dynamics simulations. In our model, the second lobe therefore has larger effective diameter, i.e. $\sigma_{BB} > 1$. For the asymmetric dumbbells with touching, rather than fused, spherical lobes, the packing fraction is given by

$$\phi = \frac{\pi N (\sigma_{\rm AA}^3 + \sigma_{\rm BB}^3)}{6V} \tag{15}$$

We used only touching spheres for our asymmetric dumbbells for a simpler model with fewer parameters, thus also simplifying the calculation of the packing fraction.

2.2. Basin-Hopping global optimisation technique



Figure 13: A schematic representation, illustrating how the basin-hopping global optimisation technique reduces the potential energy surface to a set of basins. Image was taken from the user manual of GlOSP [78].

The basin-hopping global optimisation technique is a well established method for searching the potential energy surface and optimising the structure of finite cluster systems [79–82]. In this algorithm, one starts with an arbitrary configuration, which when subjected to local minimisation, gives the current minimum. In a basin-hopping step, a new configuration is generated by randomly displacing the translational and rotational coordinates of the particles, and this configuration is subjected to local minimisation to obtain a new minimum. The proposed step from the current minimum to the new minimum is accepted or rejected based on the Metropolis acceptance criteria [83], using a fictitious temperature. The technique relies upon a hypersurface deformation method, which effectively reduces the potential energy surface (PES) to a set of minima, without changing their energies from the orginal PES, as depicted in Figure 13. If the basin-hopping step is accepted, the new minimum becomes the current minimum for the next step, otherwise the current minimum remain unchanged. In a basin-hopping run, this is repeated for a set number of steps and certain number of low energy minim visited during the run are saved to obtain the global minimum as the lowest lying minimum on the PES. A benefit of the basin-hopping technique, as opposed to a Monte Carlo algorithm for thermodynamic sampling, is that the step size that is utilised can be much bigger and the detailed balance need not be obeyed. Since the objective is to explore the PES, large step sizes are indeed used.

2.3. Brownian Dynamics simulations

2.3.1. Brownian Dynamics for spherical particles

Brownian Dynamics (BD) is a useful technique to observe the rheological behaviour of colloidal dispersions. The colloidal particles are much larger than the suspending fluid molecules, meaning the dynamics of the fluid can be reduced to a random force acting on the dispersed particles. BD is derived from the Langevin equation (eq. (16)) at the overdamped limit where inertia isn't taken into account, meaning the $\ddot{\mathbf{R}}(t)$ term vanishes (eq. (17)). The following methodology takes reference from the text book "Computer Simulation of Liquids" by Allen and Tildesley [84].

$$\ddot{\boldsymbol{R}}(t) = \boldsymbol{F}_{I}(t)/m + \boldsymbol{F}_{S}(t)/m - \zeta \dot{\boldsymbol{R}}(t)$$
(16)

$$\boldsymbol{F}_{I}(t)/m + \boldsymbol{F}_{S}(t)/m - \zeta \dot{\boldsymbol{R}}(t) = 0$$
(17)

where m is the mass of the particle, $\mathbf{R}(t)$ is the position of the particle at time t, $\mathbf{F}_{I}(t)$ is the interparticle force experienced by the particle, $\mathbf{F}_{S}(t)$ is the stochastic force implicitly modelling the Brownian motion of the particle due to the solvent, and ζ is the friction coefficient.

The overdamped Langevin equation can be rearranged (eq. (18)) to calculate the velocity of the particles in the system. This equation can be used to calculate the displacement a particle experiences over a set time period, Δt .

$$\dot{\boldsymbol{R}}(t) = (\boldsymbol{F}_I(t) + \boldsymbol{F}_S(t))/m\zeta \tag{18}$$

The propagation of a particle over a time step, Δt , is defined by

$$\boldsymbol{R}(t + \Delta t) = \boldsymbol{R}(t) + (\boldsymbol{F}_{I}(t) + \boldsymbol{F}_{S}(t))\Delta t/m\zeta$$

$$\zeta = k_{B}T/mD_{0}$$
(19)

where D_0 is the diffusion coefficient of a sphere at infinite dilution and k_B is the Boltzmann constant.

The stochastic force, $F_S(t)$, has an average value of zero,

$$\left\langle \boldsymbol{F}_{S}\right\rangle =0\tag{20}$$

where $\langle ... \rangle$ denotes an average over time. The stochastic force also has no correlation in time,

$$\langle \boldsymbol{F}_{S}(0)\boldsymbol{F}_{S}(t)\rangle = \lambda\delta(t)$$
 (21)

where λ defines the strength of the random force and $\delta(t)$ is a Dirac delta function. The Dirac delta function denotes the virtually instantaneous decay in the auto-correlation function which occurs due to the suspending fluid fluctuations occurring at a much faster timescale than the Brownian particle. Effectively, the Dirac delta function in time implies that there is no correlation between impacts at any two distinct times.

The strength of the stochastic force, λ , can be determined from the mean squared velocity of the system. First we use the formal solution for the Langevin equation

$$\dot{\boldsymbol{R}}(t) = e^{-t/\tau^{S}} \left(\dot{\boldsymbol{R}}(0) + \frac{1}{m} \int_{0}^{t} d\tau e^{t/\tau^{S}} \boldsymbol{F}_{S}(\tau) \right)$$
(22)

where τ^s is the relaxation time of Brownian motion.

We can square equation (22) and take the ensemble average [85]

$$\langle \dot{\boldsymbol{R}}^2 \rangle e^{2t/\tau^S} = \dot{\boldsymbol{R}}^2(0) + \frac{2}{m} \int_0^t d\tau e^{t/\tau^S} \langle \boldsymbol{F}_S(\tau) \rangle + \frac{1}{m^2} \int_0^t d\tau' \int_0^t d\tau e^{(\tau+\tau')/\tau^S} \langle \boldsymbol{F}_S(\tau) \boldsymbol{F}_S(\tau') \rangle$$

$$(23)$$

The first integral vanishes due to the $\langle \boldsymbol{F}_{S}(\tau) \rangle$ term. The second integral is calculated using the trace of $\langle \boldsymbol{F}_{S}(\tau) \boldsymbol{F}_{S}(\tau') \rangle$

$$\left\langle \dot{\boldsymbol{R}}^{2}(t) \right\rangle = \frac{3\lambda}{2m\zeta} + \left(\dot{\boldsymbol{R}}^{2}(0) - \frac{3\lambda}{2m\zeta} \right) e^{-2t/\tau^{S}}$$
(24)

If we go to the limit of infinite time then the exponential term becomes zero leaving us with

$$\lim_{t \to \infty} \left\langle \dot{\boldsymbol{R}}^2(t) \right\rangle = \frac{3\lambda}{2m\zeta} \tag{25}$$

Equipartition theorem can then be used to be substituted into equation (25) to obtain the definition of λ .

$$\frac{1}{2}m\langle \dot{\mathbf{R}}^2 \rangle = \frac{3}{2}k_B T$$

$$\lambda = 2\zeta k_B T$$
(26)

This means that the stochastic force over a timestep, Δt , becomes

$$\left\langle \boldsymbol{F}_{S}(0)\boldsymbol{F}_{S}(t)\right\rangle = \frac{\left\langle \boldsymbol{F}_{S}(0)\boldsymbol{F}_{S}(\Delta t)\right\rangle}{\Delta t} = \frac{2\zeta k_{B}T\delta r}{\Delta t}$$
(27)

where δr denotes a random number of Gaussian distribution with zero mean and unit variance.

According to equation (19) the displacement due to the random force is given as

$$\Delta R_S(\Delta t) = \frac{\boldsymbol{F}_S(t)\Delta t}{m\zeta} \tag{28}$$

The mean square displacement can now be derived as

$$\left\langle R_S(0)R_S(t)\right\rangle = \left\langle \boldsymbol{F}_S(0)\boldsymbol{F}_S(t)\right\rangle \left(\frac{\Delta t}{m\zeta}\right)^2 = \frac{2k_B T \Delta t \delta r}{m\zeta} = 2D_0 \Delta t \delta r \tag{29}$$

Equation (19) can now be reduced to the propagation algorithm we use in our Brownian dynamics program.

$$\boldsymbol{R}(t + \Delta t) = \boldsymbol{R}(t) + \frac{\boldsymbol{F}_{I}(t)\Delta t}{m\zeta} + \sqrt{2D_{0}\Delta t}\delta r$$
(30)

2.3.2. Brownian Dynamics for dumbbell-shaped particles

There is need to adapt the methodology to correctly propagate dumbbell-shaped particles using Brownian Dynamics. The following adapted methodology takes reference from the work of Heptner and Dzubiella [69].

The dumbbell particle positions are stored using a vector at the centre of mass (COM) of the dumbbell. Due to the axis-symmetric nature of the dumbbell this COM vector is then split into position vectors that are perpendicular and parallel to the direction along the axis through which the centre of the dumbbell lobes are connected (which we designate the z-axis).

$$\boldsymbol{R}_{i}(t) = \boldsymbol{R}_{i,\perp}(t) + \boldsymbol{R}_{i,\parallel}(t)$$

$$\boldsymbol{R}_{i,\parallel}(t) = [\boldsymbol{u}_{i}(t) \cdot \boldsymbol{R}_{i}(t)]\boldsymbol{u}_{i}(t)$$
(31)

where $\boldsymbol{u}_i(t)$ is the unit vector along the z-axis.

The force that each particle experiences is then split in the same way.

$$\boldsymbol{F}_{i}(t) = \boldsymbol{F}_{i,\perp}(t) + \boldsymbol{F}_{i,\parallel}(t)$$

$$\boldsymbol{F}_{i,\parallel}(t) = [\boldsymbol{u}_{i}(t) \cdot \boldsymbol{F}_{i}(t)]\boldsymbol{u}_{i}(t)$$
(32)

The dumbbell experiences force acting upon it from directions perpendicular and parallel to the z-axis. The Brownian Dynamics propagation for the particle position is then adjusted from the isotropic form accordingly.

$$\boldsymbol{R}_{i,\parallel}(t+\Delta t) = \boldsymbol{R}_{i,\parallel}(t) + \Delta t \frac{D_{\parallel}}{k_B T} \boldsymbol{F}_{i,\parallel}(t) + \delta r_{i,\parallel} \boldsymbol{u}_i(t)$$

$$\boldsymbol{R}_{i,\perp}(t+\Delta t) = \boldsymbol{R}_{i,\perp}(t) + \Delta t \frac{D_{\perp}}{k_B T} \boldsymbol{F}_{i,\perp}(t) + \delta r_{i,1} \boldsymbol{e}_{i,1}(t) + \delta r_{i,2} \boldsymbol{e}_{i,2}(t)$$
(33)

where $\boldsymbol{e}_{i,2}(t)$ and $\boldsymbol{e}_{i,2}(t)$ are unit vectors perpendicular to the z-axis unit vector, $\boldsymbol{u}_i(t)$. $\delta r_{i,\alpha}$ (α being ||, 1, or 2) is the random force describing the brownian motion acting on the particles. The random force is a Gaussian distributed random number which has zero mean and a variance of $\sqrt{2D\Delta t}$ where D is either the parallel, D_{\parallel} , or perpendicular, D_{\perp} , diffusion coefficients depending on α . The diffusion coefficients are obtained using the Rotne-Prager-Yamakawa tensor, explained in more detail below with benchmarking data.

Due to the anisotropy of the dumbbell particle we must also propagate the orientation of the particles. This propagation is done by calculating the torque that the particle experiences due to the perpendicular force,

$$\boldsymbol{T}_{i}(t) = \frac{\sigma}{2} L^{*} \boldsymbol{u}_{i}(t) \times (\boldsymbol{F}_{(i,2),\perp}(t) - \boldsymbol{F}_{(i,1),\perp}(t))$$
(34)

and taking the cross product of the torque and z-axis unit vector.

$$\boldsymbol{u}_{i}(t+\Delta t) = \boldsymbol{u}_{i}(t) + \Delta t \frac{D_{r}}{k_{B}T} \boldsymbol{T}_{i}(t) \times \boldsymbol{u}_{i}(t) + \delta x_{1} \boldsymbol{e}_{i,1}(t) + \delta x_{2} \boldsymbol{e}_{i,2}(t)$$
(35)

Here, $\delta x_{i,n}$ is a Gaussian distributed random number which has zero mean and a variance of $\sqrt{2D\Delta t}$ where D is the rotational diffusion coefficient, D_r .

2.3.3. Lees-Edwards shearing boundary

To apply an external shear to the system we employ the Lees-Edwards shearing boundary to replace the standard periodic boundary conditions [86]. Lees and Edwards propose two ways of applying the boundary, the angling of the simulation box or a sliding box scheme [86]. The sliding box method is preferred for long BD simulations so as to avoid very acute angles for the box as the simulation proceeds [84]. The sliding box Lees-Edwards shearing boundary has been used extensively with most discrete particle simulations including BD [69, 87, 88].

In the sliding box method, when a particle leaves the central image in the shear velocity gradient direction, it is placed on the opposite side of the box with an added displacement, ΔR_x , in the flow direction relative to the rate of shear that is imposed on the system. $\Delta R_x = \Delta t \dot{\gamma} L$, where L is the length of the central simulation box. The displacement is reversed for particles crossing the opposite boundary. This method creates sliding layers of periodic images and, with enough simulation time, will allow the system to reach a non-equilibrium steady state. On top of this shearing periodic boundary condition, we must account for shear within the propagation itself [84]. The shear flow in this case is a laminar couette flow, or a flow with a symmetric flow velocity gradient in one plane, in our case the xy-plane. This means the shear only affects the translation of the particle in the x-direction, scaled by the previous position of the particle in the y-axis.

For the propagation of a spherical system in BD, we take equation (30) and simply add the shear displacement, as seen in equation (36).

$$\boldsymbol{R}(t+\Delta t) = \boldsymbol{R}(t) + \frac{\boldsymbol{F}(t)\Delta t}{m\zeta} + \sqrt{2D_0\Delta t}\delta r + \Delta t\dot{\gamma}(t)R_y(t)\boldsymbol{e}_x$$
(36)

For the dumbbell system the parallel and perpendicular translational propagation are calculated the same as the equilibrium system. The addition shear displacement is added to the final centre-of-mass translational propagation, equation (31).

$$\boldsymbol{R}_{i}(t+\Delta t) = \boldsymbol{R}_{i,\perp}(t+\Delta t) + \boldsymbol{R}_{i,\parallel}(t+\Delta t) + \Delta t \dot{\gamma}(t) \boldsymbol{R}_{y}(t) \boldsymbol{e}_{x}$$
(37)

The orientation of the dumbbell particle is propagated in the same way as the equilibrium system with the addition of an adjusted torque calculation that includes both the previous inter-particle contribution and the contribution from the external shear flow.

$$\boldsymbol{u}_{i}(t+\Delta t) = \boldsymbol{u}_{i}(t) + \Delta t \frac{D_{r}}{k_{B}T} \boldsymbol{T}_{i}^{\dot{\gamma}}(t) \times \boldsymbol{u}_{i}(t) + \delta x_{1} \boldsymbol{e}_{i,1}(t) + \delta x_{2} \boldsymbol{e}_{i,2}(t)$$
(38)

$$\boldsymbol{T}_{i}^{\dot{\gamma}}(t) = \boldsymbol{T}_{i}(t) - \frac{k_{B}T}{D_{r}} [\boldsymbol{u}_{i}(t) \times E(t) \cdot \boldsymbol{u}_{i}(t)]$$
(39)

The contribution of the shear flow is calculated using a simple rate-of-strain tensor that limits the contribution, again, to the xy-plane.

$$E(t) = \dot{\gamma}(t) \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(40)

2.3.4. Cell list with shear

We implemented a cell list to be used with our BD program to improve the efficiency and therefore speed of the simulations. The cell list implementation used was taken from the book, "Computer Simulation of Liquids" by Allen and Tildesley [84].

The "raw" program uses a cut off distance for the pair potential calculation to ensure that time isn't wasted calculating the potential energy for two particles that are sufficiently distant that the energy, and therefore force, would be calculated to a value of zero. This cut off is determined by plotting the equation for potential energy and picking a sufficient distance for the tail to reach a near-zero value. For a Lennard-Jones system with the exponent n = 6, we would use a cut off of 2.5σ which would give an energy value of roughly $1/60^{th}$ of the depth of the attractive well, or ϵ .

Although the use of a cut off distance speeds up the simulation greatly, we still have to go through every pair of particles in the whole simulation box and calculate the distance between them to compare against the cut off. This means we must go through N(N-1) combinations, which for even a 500 particle system would mean hundreds of thousands of pairs. The Lennard-Jones system with the exponent n = 6, even at high density, would have less than 50 particles that would possibly be within a sufficient distance to each other to impart a non-zero force. This means that we should only have to calculate 50N pairs to probe the whole system, which for a 500 particle system would equate to almost a 10 fold reduction in the number of pair distances calculated.

Cell list enables us to tackle this issue by splitting the simulation box into $M \times M \times M$ cubic cells. The edge length of each cell must be greater than the cut off distance of the potential. Cell list is most optimal when M is given as the maximum number of cells that can fit along the edge of the simulation box. The particles are sorted into the cells at the beginning of every step and for each particle the pair distance is only calculated for the other particles in the cell and the particles in half of the adjacent cells. The adjacent cells are the 26 cells surrounding a central cell in a $3 \times 3 \times 3$ cube of cells. Only half of the adjacent cells are needed to be taken into account due to the use periodic boundaries, meaning we can just take the top layer of 9 cells and 4 cells in the middle layer leading to 13 neighbouring cells. There are approximately N/M^3 particles per cell with 14 cells to consider, meaning a considerable reduction in the number of pairs compared to the "raw" program.

To correctly use cell list with a Lees-Edwards shear boundary, the top layer of cells in the simulation box in the direction of the velocity gradient are treated differently (assuming a shear in the xy-plane, the "top layer" would be the top y layer). Each cell in this layer considers the same 13 adjacent cells as before with the addition of a row of cells in the

x-direction (or the direction of shear) for the top layer of neighbours, above the cell in question. We now have 12 neighbour cells in this top layer, therefore 16 neighbour cells in total. This top layer of 12 cells is then given an adjustment in the x-direction dependent on the strain on the system (defined by the shear rate and time). This treatment ensures that we look at all the relevant particles when a Lees-Edwards shear boundary with the sliding box method is being used.

2.4. Reduced units

As we are using a simple pair potential to model are particles, we can use a few parameters to define our whole system, a common practice in computational techniques. In the generalised Lennard-Jones potential, we can define the units energy, length and mass in the system by ϵ, σ , and m respectively. From these parameters, we can define the unit of temperature as ϵ/k_B , where k_B is the Boltzmann constant. From these base units of the system we can reduce the static and dynamic properties of the system to dimensionless properties such as,

$T^* = k_B T / \epsilon$
$P^* = P\sigma^3/\epsilon$
$ ho^* = ho \sigma^3$
$U^* = U/\epsilon$
$F^* = F\sigma/\epsilon$

As we are using Brownian Dynamics, we define the unit of time in our system as $\tau = \sigma^2/D_0$. D_0 is the diffusion coefficient for a single sphere at infinite dilution obtained from the Stokes-Einstein relations, $D_0 = \frac{k_B T}{3\pi\eta_0\sigma}$, with a solvent viscosity η_0 . Note here that to maintain the correct units in our dumbbell particle propagation, discussed previously in this chapter, we must normalise our diffusion coefficients by D_0 .

By using reduced units, we can lower the computational cost of calculations by setting the base unit of ϵ , σ , m and η_0 to unity, which allow us to simply the equations in the propagation of the system. If a more complex model is required with many more parameters the use of reduced units may not significantly affect simulation times.

Once the simulation results are obtained, the reduced properties can be translated back into real units to be used in experimental studies. For example, in a system of Argon where $\sigma = 3.405$ Å, m = 0.03994 g/mol, and $\epsilon/k_B = 119.8$ K, a simulation using a reduced temperature of $T^* = 1$, reduced pressure of $P^* = 1$, and a timestep of $\Delta t = 0.001\tau$ is equivalent to a real temperature of 119.8 K, real pressure of 41.9 MPa, and a timestep of 2.18 fs.

2.5. Methods for data analysis

2.5.1. Radial distribution function

The spatial arrangement of the system can be analysed using the radial distribution function (RDF). The RDF measures the probability of finding a particle at a particular distance away from a reference particle averaged over all particles in the system over any number of configurations along the simulation trajectory. The probability function g(r)represents the probability of finding a particle in a shell with thickness dr at a distance r.

$$g(r) = \frac{N_s}{V_s \rho}$$

$$V_s = \frac{4}{3}\pi (r+dr)^3 - \frac{4}{3}\pi r^3$$
(41)

where N_s is the number of particles in the shell, V_s is the volume of the shell, and ρ is the density of the system.

The RDF is a simple tool to determine the structural order that the system possesses. If in the gas phase, no order should be observed and so no peaks in the RDF. In the liquid phase some short-range order would be observed but for the order to vanish at long range. In the solid phase we would expect to see regular peaks throughout the RDF regardless of range. Where no order is observed, we should expect the probability function g(r) to have a value of 1 as the density of particles in each shell should be the same as the overall system density.

2.5.2. Time-correlation functions

Time-correlation functions are a useful way of representing time-dependent data and are a common tool to obtain dynamic properties of a system. They can be used whenever we analyse the statistical behaviour of a time-dependent variable, such as A(t). The function measures the correlation of the fluctuations of the variable, A(t), at different points in time, where the fluctuations, $\delta A(t)$, are defined as

$$\delta A(t) = A(t) - \langle A \rangle \tag{42}$$

where $\langle A \rangle$ is the time-averaged value of the variable. The time-correlation function of a variable is then defined as the time-averaged product of two fluctuations at points in time

$$C(t) = \frac{1}{\tau} \int_0^\tau \delta A(s) \delta A(s+t) ds$$
(43)

where τ is the amount of time the correlation is averaged over, s are the time origins that are integrated over and t is the amount of time separating the two fluctuations. The time-correlation function is not bound by a specific initial time but is defined by the separation in the time between the two fluctuations. A correlation of two fluctuations at the same time is given as C(0). The generic example of a time-correlation function used here is often defined as an "auto-correlation" function, meaning the correlation is between fluctuations of a variable with itself at different points in time over the trajectory. Note, that this is not always the case but is often the case when time-correlation functions are used to obtain dynamic properties of a system.

In computer simulations, we can easily track the change in a variable over time and so can directly produce the time-correlation function of a variable. In experiment it is not always possible to directly measure the time-dependent variables where instead the data obtained is of the Fourier transform of the time-correlation function, called the spectral density. A Fourier inversion can then be performed to recover the time-correlation function.

2.5.3. Linear response theory

Linear response theory (LRT) can be used to observe the response of an equilibrium system due to an external force. When the external force is weak enough the change to the coupled internal variable of the system is proportional to the force, i.e. there is a linear relationship between the external force and the change in the internal variable. The idea behind LRT is that, for weak enough perturbations, the equilibrium fluctuations can dictate the non-equilibrium response. An example of a non-equilibrium response would be the viscosity of the system under a shear flow. We can use LRT to observe the viscosity of an equilibrium system, which will be particularly important in the work of this thesis.

For a generic example, we can describe the equilibrium system with the Hamiltonian, H_0 . The non-equilibrium system can then be described with the Hamiltonian,

$$H = H_0 - f(t)A \tag{44}$$

where the external force is given by f(t) and A denoted the internal variable coupled to the external force. The initial system is at thermal equilibrium, so we can observe ensemble averaging of the internal variable, $\langle A \rangle$. The external force is then applied at some time, t_0 , and the internal variable changes as a response, characterised by a non-equilibrium ensemble average, \overline{A} .

For a weak enough perturbation, we can approximate the non-equilibrium ensemble average of the internal variable by an expansion in powers of the external force. The approximation is to the first two terms of the expansion, given as,

$$\overline{A(t)} = \langle A \rangle + \int_{-\infty}^{\infty} R(t, t_0) f(t_0) dt_0$$
(45)

where t is the time over which the external force was applied and $R(t, t_0)$ is the response function [89]. The first term is independent of the force and can be reduced to the equilibrium ensemble average of the internal variable. The second term describes the linear response of the system away from equilibrium due to the external force, where the integration is showing that the response depends on the whole time that the perturbation is being applied. The lower limit of $-\infty$ implies that the system starts at equilibrium.

From here, two main properties of the response function come in to play. First is of causality, which states that the system cannot respond before the external force has been applied. This means that $R(t, t_0) = 0$ when $t < t_0$. We can rearrange the approximation in equation 45 to obtain the fluctuation of the non-equilibrium ensemble average of the internal variable.

$$\delta \overline{A(t)} = \overline{A(t)} - \langle A \rangle = \int_{-\infty}^{t} R(t, t_0) f(t_0) dt_0$$
(46)

The second property of the response function is that of stationarity, which states that the time-dependence of the system only depends on the difference between the time at which the force was applied, t_0 , and the time at which the observation was made, t. This means that $R(t, t_0) = R(t - t_0)$ and equation 46 becomes,

$$\delta \overline{A(t)} = \int_{-\infty}^{t} R(t - t_0) f(t_0) dt_0$$
(47)

This equation can then be rewritten to use a defined time-interval $\tau = t - t_0$, in place of the absolute time.

$$\delta \overline{A(t)} = \int_0^\infty R(\tau) f(t-\tau) d\tau$$
(48)

Comparing this final form with the result of the fluctuation-dissipation theorem [89], up to the linear term,

$$\delta \overline{A(t)} = \frac{f}{k_B T} \langle \delta A(t) \delta A(0) \rangle \tag{49}$$

it follows that the non-equilibrium response in the linear regime is related to the correlations between spontaneous fluctuations at different times as they occur in the system at equilibrium.

2.5.4. Translational diffusion

Translational diffusion can be calculated using the Green-Kubo relation of the velocity auto-correlation function. However, due to the Brownian Dynamics technique being in the overdamped limit, a velocity is not being directly calculated and so we cannot use this method. Instead, we can analyse the mean square displacement (MSD) of particles over the simulation trajectory. The relation is derived from the Einstein formula,

$$\left\langle \Delta r^2(t) \right\rangle = 2NDt \tag{50}$$

where $\langle \Delta r^2(t) \rangle$ is the mean-squared displacement (MSD) of a particle, N is the number of dimensions of the system, D is the diffusion coefficient and t is time. The MSD of a system is a measure of the movement of the particles from their starting positions over time. The diffusion coefficient obtained is the centre-of-mass diffusion coefficient, which can then be broken down for the axisymmetric dumbbell system into the parallel and perpendicular diffusion coefficients by $D_{COM} = \frac{1}{3}D_{\parallel} + \frac{2}{3}D_{\perp}$.

2.5.5. Rotational diffusion

The rotational diffusion coefficient can be calculated from the orientational auto-correlation function,

$$\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0) \rangle = e^{-2D_r t}$$
 (51)

The orientational relaxation time, τ_r , can also be derived from the rotational diffusion coefficient with the simple relationship, $D_r = \frac{1}{2\tau_r}$.

2.5.6. Stress

The stress of the system is calculated using the Irving Kirkwood stress tensor, given as $\sigma_{\alpha\beta}$ where α and β are cartesian coordinates [90]. The off-diagonal elements of the stress tensor give us the stress on the system along each cartesian plane, xy, yz and zx.

$$\sigma_{\alpha\beta} = -\frac{1}{V} \left[\sum_{i=1}^{N_p} m_i (\boldsymbol{v}_{i\alpha} \cdot \boldsymbol{v}_{i\beta}) + \sum_{i=1}^{N_p} \sum_{j>i}^{N_p} \boldsymbol{r}_{ij,\alpha} \cdot \boldsymbol{F}_{ij,\beta} \right]$$
(52)

The stress calculation must change due to the BD system being in the overdamped limit and therefore a velocity not being directly calculated. The kinetic contribution to the Irving-Kirkwood stress tensor is simply reduced using equipartition theory, to 3kT. As the kinetic term is a constant we ignore it in our stress calculation.

$$\sigma_{\alpha\beta} = -\frac{1}{V} \left[3kT + \sum_{i=1}^{N_p} \sum_{j>i}^{N_p} \boldsymbol{r}_{ij,\alpha} \cdot \boldsymbol{F}_{ij,\beta} \right]$$
(53)

The potential term of the stress tensor is proportional to the intermolecular pair virial function, $w(r_{ij})$, by

$$\boldsymbol{r}_{ij} \cdot \boldsymbol{F}_{ij} = -w(r_{ij}) \tag{54}$$

To model the dumbbell system, we utilise the site-site interactions of the dumbbell lobes. To calculate the correct potential term of the stress tensor in the site model, we must correctly calculate the intermolecular pair viral function from the site-site pair virial function, $w_{ab}(r_{ab})$, where a and b are the sites of the dumbbell. The relationship is given as

$$w(r_{ij}) = \sum_{a} \sum_{b} \frac{w_{ab}(r_{ab})}{r_{ab}^2} (\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{ij})$$
(55)

where \mathbf{r}_{ab} is the distance between the *a* site of the *i*-th dumbbell and the *b* site of the *j*-th dumbbell.

2.5.7. Equilibrium viscosity

To calculate the equilibrium viscosity we can utilise the stress auto-correlation function (SACF). At equilibrium there is no external bias on any of the cartesian planes of our cubic simulation box. Therefore, we can average the SACF over the three off-diagonal elements of the stress tensor.

$$\left\langle \sigma_{avg}(t)\sigma_{avg}(0)\right\rangle = \frac{1}{3} \Big[\left\langle \sigma_{xy}(t)\sigma_{xy}(0)\right\rangle + \left\langle \sigma_{yz}(t)\sigma_{yz}(0)\right\rangle + \left\langle \sigma_{zx}(t)\sigma_{zx}(0)\right\rangle \Big]$$
(56)

Viscosity is then obtained from the integration derived from the Green-Kubo relation of the averaged SACF, as given in equation (57).

$$\eta^* = \frac{V}{k_B T} \int_0^\infty \left\langle \sigma_{avg}(t) \sigma_{avg}(0) \right\rangle dt \tag{57}$$

2.5.8. Shear viscosity

Under an external shear, we are no longer able to utilise the Green-Kubo relation of the stress auto-correlation function. This is because the response to the external stimulus is non-linear and so the relation is no longer valid.

The shear viscosity of the system is obtained using Newton's law for viscosity. Under laminar flow, the stress of the system in the flow plane, σ_{xy} , is proportional to the shear rate, $\dot{\gamma}$, with the constant of proportionality being the shear viscosity. This can be rearranged to obtain shear viscosity.

$$\eta_{xy}^* = \frac{\sigma_{xy}}{\dot{\gamma}} \tag{58}$$

2.6. Benchmarking

As we have developed the code for the Brownian Dynamics for dumbbell particles inhouse, we must benchmark the code to be confident that the code correctly simulates the given theory. It is crucially important that we are confident in the data that we obtain from the simulations as we will be looking at new data that may not have straight forward properties. We want to be sure that any new behaviours that we observe are true observations of the theory and not products of bugs in the code. Below is some of the benchmarking data that analysed to ensure that the code is working as intended.

We benchmarked the dumbbell Brownian Dynamics code against work by Heptner and Dzubiella [69]. The simulations were of symmetric dumbbells with varying aspect ratios and packing fractions. We looked to match the properties of the equilibrium simulations between our code and data presented by Heptner and Dzubiella.

2.6.1. Benchmarking the diffusion coefficients

We are utilising the translational and rotational diffusion coefficients of a single dumbbell particle at infinite dilution for the propagation of our system using Brownian Dynamics. The coefficients are calculated using the 5th-order approximation of the Rotne-Prager-Yamakawa (RPY) tensor [91, 92]. The tensor utilises the idea that when a particle begins to move due to an applied force, flow is induced in the bulk fluid. This flow then effects the translational and rotational velocities of another particle in the system [93]. Mobility tensors can be formed relating to the translation, rotation and translationrotation coupling of the forces and velocities. The diffusion coefficients can then be derived from these mobility tensors [94]. The coefficients are then normalised by the single-sphere diffusion coefficient to maintain the correct units in our simulation.

All three diffusion coefficients are normalised by the translational diffusion of a singlesphere, $D_0 = \frac{k_B T}{3\pi\eta_0\sigma}$, to obtain the correct units in our propagation. However, for the sake of benchmarking and comparing our diffusion coefficients with known work, we have normalised the parallel and perpendicular translational coefficients by translational diffusion of a single-sphere and the rotational coefficient by the rotational diffusion of a single-sphere, $D_r^0 = \frac{k_B T}{\pi\eta_0\sigma^3}$.

Using this method, we have the parallel translational diffusion coefficient D_{\parallel}/D_0 , perpendicular translational diffusion coefficient D_{\perp}/D_0 and rotational diffusion coefficient D_r/D_r^0 .



Figure 14: A plot of the normalised parallel, perpendicular and rotational diffusion coefficients as a function of the aspect ratio of a symmetric dumbbell particle.

Figure 14 shows the normalised values calculated from the RPY tensor and is comparable

to work reported by Heptner and Dzubiella [69]. We have also given a table of the diffusion coefficients at key aspect ratio values that Heptner reported to get a direct comparison between the normalised diffusion coefficients. There is some apparent dicrepancy between the absolute numbers but this will purely be down to the slightly different methods used to calculate the coefficients. Heptner use the Shell Bead Model (SBM) which uses the RPY tensor but breaks the single particle down into lots of "beads" at the surface. This is a costly but more accurate method. Due to the computational cost we opted to instead use the 5th-order approximation of the tensor.

L^*	D_{\parallel}^{SBM}	D_{\parallel}^{RPY}	D_{\perp}^{SBM}	D_{\perp}^{RPY}	D_r^{SBM}	D_r^{RPY}
0.02	0.99	1.00	0.99	0.99	0.97	0.98
0.10	0.97	0.98	0.95	0.95	0.85	0.89
0.24	0.93	0.96	0.89	0.90	0.69	0.76
0.30	0.91	0.94	0.87	0.87	0.63	0.71

Here we observe that, in comparison to the SBM method, our RPY method has a shallower decrease in diffusion as a function of aspect ratio across all three coefficients. We believe that the discrepancy is expected from the difference in method and the program is working as intended.

2.6.2. Benchmarking the algorithm

We benchmarked the algorithm against work by Heptner and Dzubiella [69], and so have used a symmetric dumbbell system. The first form of benchmarking is through the radial distribution function (RDF) of the system. Although it is a good initial test, the RDF of a system is quite robust so it may not always be indicative of a working program. However, the initial test was very successful. As seen in Figure 15 and Figure 16, we matched the RDFs very well with the literature at $\phi_{\alpha} = 0.44$ and 0.60. This data shows the distinct change in phase behaviour of the dumbbells as the packing fraction of the system is increased. Going from $\phi_{\alpha} = 0.44$ to $\phi_{\alpha} = 0.60$, we see a clear transition from a fluid-like behaviour to a plastic crystalline behaviour. We also see in Figure 16, that as the elongation of the dumbbells increases the system becomes less crystalline.



(a) Our code

Figure 15: (a) shows our plot of RDF at $\phi_{\alpha} = 0.44$ at varying aspect ratios. (b) shows the equivalent plot given in Heptner's work.

Diffusion is a better benchmark test as it is less robust and will be more sensitive to any inconsistencies in the code. First we looked at translational diffusion. For dumbbells, there is translation perpendicular and parallel to the axis at which the two spheres of the dumbbell separate. The diffusion was calculated via the gradient of the respective mean square displacements and normalised by the translational diffusion of a single dumbbell at infinite dilution. As seen in Figure 17 and Figure 18, we have a very good match with literature for the translational diffusion constants for the system. This diffusion data shows us that the diffusion constants of the dumbbells is only loosely dependent on the



(a) Our code

Figure 16: (a) shows our plot of RDF at $\phi_{\alpha} = 0.60$ at varying aspect ratios. (b) shows the equivalent plot given in Heptner's work.

elongation of the dumbbell. This means that the shape anisotropy is not having a large impact on the diffusion of the system. We do, however, see a decrease in the diffusion constant as packing fraction (ϕ_{α}) is increased. This observation is due to the system transitioning to a more crystalline state as ϕ_{α} is increased.



Figure 17: (a) shows our plot of parallel translational diffusion at $\phi_{\alpha} = 0.22$ and 0.44 at varying aspect ratios. (b) shows the equivalent plot given in Heptner's work.

As the dumbbell is axis-symmetric, we can also look at how the dumbbell diffuses via rotation. We calculated the orientational diffusion of the dumbbell system by fitting the



Figure 18: (a) shows our plot of perpendicular translational diffusion at $\phi_{\alpha} = 0.22$ and 0.44 at varying aspect ratios. (b) shows the equivalent plot given in Heptner's work.

time evolution of the first-rank orientational auto-correlation function to an exponential decay and normalising the calculated value by the rotational diffusion of a single dumbbell at infinite dilution. When normalised in this way, it would be expected that the value of the rotational diffusion coefficient tends to 1 as the infinitely dilute regime is approached. The lowest packing fraction used in our work was $\phi_{\alpha} = 0.22$, seen in Figure 19a; it would be expected for the rotational diffusion coefficient to approach 1 as the packing fraction is further reduced. The work that we benchmarked against, seen in 19b, shows data down to the very dilute regime and sees the values of the normalised diffusion coefficients tend to 1. Our data do not appear to quantitatively match in the region of packing fraction $\phi_{\alpha} \approx 0.2$, but the qualitative trend is reproduced well.

Despite the quantitative discrepancies, we can see from Figure 19 that, unlike the translational diffusion, there is almost no dependence between ϕ_{α} and the orientational diffusion coefficient at the near-spherical limit of the dumbbells. When the shape anisotropy is increased, we see a large drop in the orientational diffusion coefficient at higher ϕ_{α} . This data suggests that packing effects are influencing how the dumbbells can rotate, which matches literature findings.



(a) Our code

(b) Image reproduced from Heptner's work

Figure 19: (a) shows our plot of orientational diffusion at varying ϕ and aspect ratios. (b) shows the equivalent plot given in Heptner's work.

It is clear from the data presented that we can find confidence in the dumbbell BD framework that we have developed. The data obtained from this program as we go forward in this work can be trusted as real observations.

2.6.3. Benchmarking the shear boundary conditions

To benchmark the Lees-Edwards shear boundary we must observe whether our code is self-consistent. To do this we first calculate the equilibrium viscosity of the system using the Green-Kubo relation to integrate the stress-stress auto-correlation function of a sufficiently long simulation with no external shear present. We can then compare the equilibrium viscosity with the shear viscosity of the same system under a low shear rate. At a sufficiently low shear rate we would expect the system to have barely moved from equilibrium and therefore be able to calculate comparable viscosities in both methods of viscosity calculation.

We have produced benchmarking data using the asymmetric dumbbell system with the parameters $\sigma_{BB} = 5$ and $\epsilon_{BB} = 0.5$ at three different system densities each with three identical simulations with different starting configurations taken from an initial equilibrated system of asymmetric dumbbell particles. the numbers can be translated easily, with the densities being absolute and packing fractions comparative. The system densities were defined by the dumbbell packing fraction, ϕ , with values of $\phi = 0.18, 0.29$ and 0.39 used here. Due to the size of the asymmetric dumbbell, these packing fractions translate to reduced densities of $\rho^* = 0.0028, 0.0044$ and 0.0060 respectively.

The interparticle force is given by the generalised Lennard-Jones potential with a Lennard-Jones exponent of n = 24. Our simulations use 500 dumbbell particles which are propagated using a timestep of $\Delta t = 1 \times 10^{-5} \tau$ and a temperature of $T^* = 0.40$.

We ran the initial equilibration for each density for 100 million steps, split into 20 million equilibration steps and 80 million production. From the 80 million production runs we selected 3 starting configurations to run our sheared systems. The sheared simulations were also run for 100 million steps with the stress of the system being calculated and printed every 10 timesteps. We are printing so often in order to gather enough steady state data to obtain a good statistical average for the viscosity calculations.

As an initial sanity check, we can say that qualitatively the viscosities are increasing with increasing density as expected.

We first ran with a shear rate of $\dot{\gamma} = 0.01$. When comparing between the equilibrium viscosity and low shear viscosity in table I, we have some particularly erroneous points,

$T^* = 0.40$	η_{eq}	$\eta_{\dot{\gamma}=0.01}$	% Error
$\phi = 0.18$			
Config. 1	0.00185	0.00186	0.7
Config. 2	0.00172	0.00196	14
Config. 3	0.00171	0.00230	34
$\phi = 0.29$			
Config. 1	0.00705	0.00671	5
Config. 2	0.00799	0.00676	15
Config. 3	0.00615	0.00697	13
$\phi = 0.39$			
Config. 1	0.0213	0.0237	11
Config. 2	0.0188	0.0266	41
Config. 3	0.0238	0.0255	7

Table I: Comparison of equilibrium viscosity, η_{eq} , against the viscosity at low shear, $\eta_{\dot{\gamma}=0.01}$, at three different starting configurations of three system densities.

like that of the second starting configuration of the $\phi = 0.39$ system with a 41% error. However, we do have some very good matching between the equilibrium and low shear viscosities, with errors as low as 0.7%. The majority of errors are below 15% which we deem a good matching when taking into account that the error between equilibrium viscosities of the same density can be up to 20%. Due to the statistical nature of the viscosity calculations, we have run our simulations for a very long time, but it seems like we may need even longer runs to guarantee the statistical averaging is giving us the correct result. We must trade some statistical accuracy with the time taken to gather the data.

Theoretically, a low enough shear rate should give a good match in viscosity to the equilibrium case. However, to calculate viscosity, the average stress of the system is divided by the shear rate. This means that the accuracy of the statistical averaging is of critical importance as we lower the shear rate. The erroneous values observed in table I could be fixed but may require an unfeasibly long simulation to get the sufficient level of

Table II: Comparison of equilibrium viscosity, η_{eq} , against the viscosity at low shear, $\eta_{\dot{\gamma}=0.1}$, at three different starting configurations of three system densities. Improved matching between the equilibrium viscosity and low shear viscosity is observed.

$T^* = 0.40$	η_{eq}	$\eta_{\dot{\gamma}=0.1}$	% Error
$\phi = 0.18$			
Config. 1	0.00185	0.00183	1
Config. 2	0.00172	0.00156	9
Config. 3	0.00171	0.00159	7
$\phi = 0.29$			
Config. 1	0.00705	0.00661	6
Config. 2	0.00799	0.00665	17
Config. 3	0.00615	0.00664	8
$\phi = 0.39$			
Config. 1	0.0213	0.0218	2
Config. 2	0.0188	0.0222	18
Config. 3	0.0238	0.0219	8

statistical averaging. To test this theory we ran the same set of simulations with a shear rate of $\dot{\gamma} = 0.1$, seen in table II, and saw much better matching of the equilibrium viscosity to low shear viscosity with every run matching within 20 % and the majority matching within 10 % error. This increase in accuracy shows that the limitation of statistical averaging is alleviated as we increase shear rate.

Following this benchmarking data, we are convinced that we have implemented the external shear correctly within our dumbbell BD framework. We are aware of the pitfalls of statistical averaging and understand that there will be some trade off with statistical averaging and simulation time. We must continue running multiple starting configurations for the same phase space to ensure that we can avoid erroneous trends and continue to monitor these trends and carefully consider the length of our production trajectories.
3. EXPLORING THE EFFECTS OF SHAPE ANISOTROPY ON THE RHEOLOGICAL BEHAVIOUR OF SUSPENSIONS OF SYMMETRIC COLLOIDAL DUMBBELLS

3.1. Introduction

Interest in the colloidal dumbbells has grown significantly in recent years. This growth is closely attributed to the advances in synthetic techniques for the dumbbell-shaped particles in the nano- and micro-scale. Several studies reveal simple techniques to fabricate dumbbell particles with control over lobe dimensions and surface chemistry [62–65, 95]. Importantly, monodispersed colloidal dumbbells can be synthesised, thus bringing experimental and computational studies closer together.

The phase behaviour of hard dumbbells is well studied by Monte Carlo simulations [66–68, 96]. The phase diagram of hard dumbbells is shown in Figure 10. Dense suspensions of these particles in the near-spherical limit with an aspect ratio L^* of less than 0.4 transition into a plastic crystal regime [66–68]. At higher aspect ratios, the plastic crystal phase is lost the phase diagram; instead a direct transition from the fluid phase to a closed-packed crystal is observed. The dynamical and rheological behaviour of colloidal dumbbells with such a rich phase behaviour has also drawn attention in recent years [69, 70].

Understanding the effects of shape anisotropy on the rheological behaviour of suspensions of colloidal dumbbells in the presence of depletion, which has emerged as a versatile tool for controlling attractive interactions between colloidal particles in a suspension and hence its microstructures, is of both fundamental and practical interests. In this context, the aim of this computational study was to investigate the effects of shape anisotropy on the rheological behaviour of dense suspensions of symmetric colloidal dumbbells when depletion is in operation. To this end, we considered a model system of symmetric colloidal dumbbells for a range of aspect ratios, not limiting to the near spherical regime, at three different effective packing fractions. We investigated the dynamical properties of the system at equilibrium before studying the system under steady shear.

3.2. Discussion

3.2.1. Dynamical properties

We used Brownian Dynamics simulations to investigated systems of colloidal symmetric dumbbell suspensions interacting via depletion attractions, modelled by the generalised Lennard-Jones pair potential. We studied the system at a reduced temperature of $T^* = 1$ for a range of aspect ratios from $L^* = 0.2$ to 0.8, over a range of effective packing fractions, $\phi_{\alpha} = 0.497, 0.524$ and 0.550. The chosen effective packing fractions fall within the fluid phase of the phase diagram for hard symmetric dumbbells practically for all investigated L^* , as reported by Marechal and Dijkstra [68]. In order to study the effect of shape anisotropy of the dumbbells on the microstructure and rheological behaviour of the system, we looked to study a phase space without the influences of a phase boundary. It is important to note here that we are utilising the *effective* packing fraction , $\phi_{\alpha} = \frac{\pi N \alpha}{6V}$, the geometric factor α , which is a function of L^* , was included to take into account the overlap caused by fused lobes. Such a choice allows us to investigate the effects of shape anisotropy without being convoluted by the effects of a concomitant change in the packing fraction.

Figure 20 shows the radial distribution functions, g(r), for the system of the symmetric colloidal dumbbells for a range of aspect ratios, computed in terms of their centres of mass, at the highest packing faction ϕ_{α} simulated. It is clear from the figure that there is no long-range order and the system is in the fluid phase for all the aspect ratios. Although the data for only the highest packing fraction simulations are shown in the figure, similar behaviour was observed for the systems of lower packing fractions. As seen in the figure,



Figure 20: Centre-of-mass radial distribution functions for the systems of symmetric colloidal dumbbells with different aspect ratios at an effective packing fraction of $\phi_{\alpha} = 0.550$. The schematics inset in the plot suggest the pair configurations that correspond to the peaks that they point to.

there are four main configurations that a pair of symmetric dumbbells can fall into.

First, an 'X' configuration where the dumbbells are on top of each other, oriented perpendicular to each other with respect to the axis of cylindrical symmetry which is seen as a small shoulder at a separation distance below σ . The shoulder increases as the elongation of the dumbbell is increased due to the increased space between the two lobes of the dumbbell allowing for a closer centre-of-mass interaction than possible for lobe-tolobe interactions. The second configuration is the side-by-side configuration where the dumbbell pair are next to each other, oriented parallel to each other with respect to the axis of cylindrical symmetry, seen at a separation distance of around σ . As L^* increases, the shoulder at lowest aspect ratio becomes gradually more pronounced resolving into a smaller peak. The reasoning for this is due to the proximity of the large peak for the third configuration, which is a 'T' configuration where the dumbbells are oriented perpendicular to each other, as with the 'X' configuration, but in the same plane as each other, forming a 'T' shape. The peak corresponding to the 'T' configuration appears at a separation distance of around $\sigma + \frac{1}{2}L^*$, due to the centre-of-mass of the dumbbells separating increasingly as elongation of the dumbbell increases. The final notable configuration is the end-to-end configuration of a pair of dumbbells, corresponding to the emerging shoulder past the large peak. The shoulder representing the end-to-end configuration emerges at a distance of roughly $\sigma + L^*$. Unlike the separation distance of the 'T' configuration, which is only affected by the elongation of one of the dumbbells, the end-to-end configuration separation distance is effected by the elongation of both dumbbells in the pair.

The RDF data suggests that the low aspect ratio system is dominated by parallel and 'T' configurations. As aspect ratio increases the shoulders for the 'X' and end-to-end configurations become much more pronounced, reducing but not eliminating the dominance of the other two configurations.

The static structure factor, $S(\mathbf{k})$, is a quantitative measure of how the structure of a system would scatter incident radiation, where \mathbf{k} is the scattering vector. Effectively, the static structure factor is another way of quantifying the translational order in the system. $S(\mathbf{k})$ can be calculated via the Fourier transform of the radial distribution function, but can also be calculated directly from the inter-particle distances by

$$S(\boldsymbol{k}) = \frac{1}{N} \left\langle \sum_{i}^{N} \sum_{j}^{N} \exp(-i\boldsymbol{k}(\boldsymbol{r}_{i} - \boldsymbol{r}_{j})) \right\rangle$$
(59)

In the systems considered here, the particles are placed in a cubic box with an edge length

of $L = V^{1/3}$ and with periodic boundary conditions imposed. Given this, the wavevector is defined as: $\mathbf{k} = \Delta k(n_x, n_y, n_z)$, where $\Delta k = 2\pi/L$ and $n_x, n_y, n_z = -n_k, ..., -1, 0, 1, ..., n_k$. Additionally, the structure factor can be expressed as a function of the magnitude of the wavevector: $k = |\mathbf{k}|$; where wavevectors are grouped together if they fall within the range [k, k + dk] and are averaged to give S(k) [97].



Figure 21: Static structure factor for the system of symmetric colloidal dumbbells with different aspect ratios at an effective packing fraction of $\phi_{\alpha} = 0.550$.

Figure 21 shows the static structure factor for the same system as for the RDF analysis. Although only the highest packing fraction is shown, the trends were similar in the other packing fractions studied. First of all, it must be said that the systems, as seen in the RDF data, show no long-range order. However, there is a clear decrease in the height of the first peak of the structure factor as the aspect ratio of the dumbbell is increased. Chong and Gotze [98] studied the hard dumbbell system using Mode-Coupling Theory and observed a non-monotonic trend for the static structure factor as a function of elongation. It was shown that the centre-of-mass correlations were the governing factor for the low aspect ratio regime, causing a drop in the peak intensity as the dumbbell was elongated. However, for the high aspect ratio regime, the angular correlations became dominant in governing the peak intensity of the static structure factor and an increase in the peak heights were seen. The interplay between centre-of-mass and angular correlations caused a non-monotonic trend. We do not see such a trend in the static structure factor of our system and so we can most likely conclude that the angular correlations of the dumbbells are not affecting the static structure factor of this system and we are only observing the centre-of-mass correlations which decrease as elongation of the particles increase.

Figure 22 shows the translational and rotational diffusion coefficients for the systems as a function of the aspect ratio L^* at all three packing fractions. For a given L^* , the translational diffusion coefficient is calculated from the slope of the linear regime of the curve obtained by plotting the mean-squared displacement as a function of time. D_{COM} , D_{\parallel} and D_{\perp} are obtained by considering the displacement for the centre-of-mass, and its components resolved along the directions parallel and perpendicular to the axis of elongation of the dumbbell, respectively. As expected from what is known for hard dumbbell systems [69, 70], the general trend of a decreasing diffusion coefficient with increasing packing fraction is apparent.

Figure 22a shows the rotational diffusion coefficient, D_r ; calculated by fitting the timedependence of the orientational correlation function to an exponential decay and obtaining the corresponding time constant. It is observed that D_r monotonically decreases with L^* at all three packing fractions, with D_r dropping by as much as 70% as L^* is increased from 0.2 to 0.8. Given that the effective packing fraction is the same across the aspect ratio range studied, the slowdown in rotational dynamics is caused solely by an increase in



(a) Rotational diffusion coefficient



(b) Translational parallel diffusion coefficient



(c) Translational perpendicular diffusion coefficient

(d) Translational centre-of-mass diffusion coefficient

Figure 22: Translational and rotational diffusion coefficients for the systems of symmetric colloidal dumbbells as the aspect ratio L^* is varied at three packing fractions. Error bars are included from three separate simulation runs; however, the error is insignificant.

shape anisotropy hindering the rotation due to an increasing excluded volume, rather than increased density. One reason for the decrease in the rotational diffusion coefficient, as the particles become more elongated, is the increase in excluded volume causing difficulty in performing tumbling rotations. Notwithstanding the shape anisotropy, it can be expected that the barrier to log-rolling rotation, or rotation around the cylindrical axis of the symmetric dumbbell, remains unaffected. However, the tumbling rotation, or rotation perpendicular to the cylindrical axis, is hindered as the excluded volume is increased. The monotonic trend in rotational diffusion seen here suggests that there is an increase in angular correlation of the system as the elongation of the dumbbell is increased. Although the change in angular correlation is seen in the rotational diffusion it does not seem to affect the static structure factor of the system as seen in the literature for a hard dumbbell system [98].

The translational diffusion has only a weak dependence on L^* , meaning that the shape anisotropy does not significantly affect the movement of the particles in the system. This could imply that the shape anisotropy does not significantly affect the translational friction in the system, however, as BD is an implicit solvent technique and lacks information on the hydrodynamic behaviour of the system we can not make any concrete claims on translational friction experienced by these systems [99].

The rotational diffusion coefficient, D_r , of the colloidal dumbbells in the suspensions decreases with increasing L^* regardless of their volume fraction because the excluded volume of a particle increases with increasing elongation. However, the translational diffusion coefficients show a similar trend only at longer elongation. At smaller elongation, the translational diffusion coefficients increase with increasing L^* , resulting in a nonmonotonic behaviour. The reversal of the trend at smaller elongation is due to enhanced density correlation due to the effects of forces derived from the interactions between sites at smaller separation, as apparent in Figure 23. From Figure 21, we see that the height of the first peak of static structure factor diminishes with increasing L^* showing a decay in the strength of the density correlation. Hence, the excluded volume effect takes over beyond an intermediate value of L^* .

Figure 23 shows the average energy per particle in the system as a function of the aspect ratio of the symmetric dumbbells. As the aspect ratio is increased, the average energy per



Figure 23: Average energy per particle for the system of symmetric colloidal dumbbells as the aspect ratio L^* is varied at three packing fractions.

particles becomes significantly less negative before it reaches a plateau and eventually dips again. The pair energy between the symmetric dumbbells draws contributions from the interactions between sites located at the centres of lobes. With short-range interactions at play, these contributions become weaker as the separation between the lobes increases with increasing aspect ratio, resulting in a plateau. The slight dip from this plateau observed at large aspect ratios is presumably due to closer approach between centres of mass of the dumbbells, as reflected in the RDF shown in Figure 20. The much stronger attractive interactions experienced at lower aspect ratios cause enhanced density correlations which effect the dynamics of the dumbbell particles.

We calculated the shear viscosity, η^* , at equilibrium using the Green-Kubo relation of the stress auto-correlation function, averaging over the three cartesian planes of 3D space. Figure 24 shows η^* as a function of L^* at the three packing fractions studied. There is a clear increase in viscosity as the packing fraction of the system is increased, observed in the literature for hard sphere and hard dumbbell systems [69, 100]. A non-monotonic dependence on L^* is also observed for the shear viscosity of the system at equilibrium. The non-monotonic trend as a function of L^* exhibited by the shear viscosity is consistent with the translation diffusion coefficient following the Stokes-Einstein relationship, which states that the translational diffusion coefficient decreases with increasing shear viscosity.



Figure 24: Shear viscosity for the systems of symmetric colloidal dumbbells as a function of the aspect ratio L^* at three packing fractions. Error bars are included from three independent simulations.

The shear viscosity is governed by the timescale of shear stress autocorrelation, which is in turn related to density fluctuations. The static structure factor contains information on density fluctuations. The first peak of S(q) is primary governed by the centre-of-mass density fluctuations. The growth of the height of the first peak with decreasing L^* is an indication of enhanced density correlation due to the effects of forces derived from the interactions between sites at smaller separation. On the other hand, dynamics slow down with increasing L^* . Hence, the shear viscosity shows a non-monotonic variation with L^* , with a minimum at an intermediate value of L^* . Stronger correlations dominate at smaller elongation and slow decorrelations dominate at larger elongation. Our results show that the translational diffusion coefficient exhibits a non-monotonic variation with the aspect ratio mirroring the shear viscosity, being consistent with the inverse relationship between translational diffusion and shear viscosity. However, the rotational diffusion coefficient exhibits a monotonic behaviour, decreasing with increasing aspect ratio. This set of observations is a manifestation of translational-rotational decoupling. The non-monotonic variation is apparent due to competition between stronger correlations at low aspect ratio and slower decorrelations at high aspect ratio. The translational diffusion follows this trend whereas the rotational diffusion does not, meaning the slowdown in dynamics is more dominant in the rotational degrees of freedom. The exact origins of the decoupling behaviour will be key in fully understanding the dynamics of the system and will require further investigation following this work.

3.2.2. Non-equilibrium conditions

A steady external shear flow was applied to the system of symmetric colloidal dumbbells to investigate the effect of shape anisotropy on the rheological response of the system. Figure 25a shows how the shear viscosity of the system, at an effective packing fraction of $\phi_{\alpha} = 0.550$, varies with the aspect ratio at a range of different shear rates. It is evident that the non-monotonic dependence of the shear viscosity on L^* persists even at the highest shear rate, suggesting that this dependence is a robust attribute of the system.

Figure 25b shows a shear thinning response to the applied external shear, meaning the viscosity decreases with increasing shear rate. The shear thinning behaviour appears strongest for the highest aspect ratio dumbbell system and more pronounced in the low aspect ratio regime compared to that of the median. Although only the system with

the highest effective packing fraction is shown here, all three effective packing fractions demonstrated similar results.



Figure 25: Shear viscosity of the suspensions of symmetric colloidal dumbbells under shear flow for different aspect ratios at the effective packing fraction $\phi_{\alpha} = 0.550$. (a) Shear viscosity as a function of the aspect ratio L^* at different shear rates; (b) Shear viscosity as a function of the shear rate on a log-scale for three different aspect ratios spanning the range studied.

It is important to note here that the shear viscosity reported for the lowest shear rate is slightly higher that the equilibrium viscosity reported above. For example, the system with dumbbells of an aspect ratio of $L^* = 0.2$ had an equilibrium viscosity, η^* , of roughly 1.9 and a shear viscosity, η^*_{xy} , of roughly 2.05 at the lowest shear rate of $\dot{\gamma} = 0.1$. The shear and equilibrium viscosities were calculated differently. The equilibrium viscosity was calculated using the Green-Kubo relation of the stress auto-correlation function, whereas the shear viscosity was calculated using Newton's law for viscosity. Due to the differences in methods and the heavily statistical nature of the calculations, it is difficult to confirm whether the initial increase in viscosity is a true observation or statistical error and most likely leaning to the latter.

Figure 26 shows the RDF analysis for the dumbbell system at a density of $\phi_{\alpha} = 0.550$ at the three aspect ratios studied in the shear regime over a range of shear rates. The



Figure 26: Radial distribution functions between the centre-of-masses of the symmetric dumbbells of systems under shear at a packing fraction of $\phi_{\alpha} = 0.550$. The plots show the full range of shear rates used on the system at three aspect ratios, (a) $L^* = 0.2$, (b) 0.5, and (c) 0.8.

RDF plot for the $L^* = 0.2$ system suggests there is very little microstructural change at the near-spherical regime. The high aspect ratio regime represented by the system of $L^* = 0.8$ shows a noticeable change in the local microstructure of the dumbbell system as the external shear is applied. The peak corresponding to the side-by-side configuration of a pair of dumbbells increases in intensity as shear rate increases. The shoulder that appears due to the end-to-end configuration also becomes more apparent as the shear rate applied to the system increases. The peak corresponding to the 'T' configuration decreases. This suggests that the system is moving towards a microstructure where the dumbbells are aligning parallel to each other with respect to the axis of symmetry. The system with the median shape anisotropy of $L^* = 0.5$ shows the same trends as observed in the high aspect ratio system, though to a lesser extent.



Figure 27: Comparison of probability densities along the cartesian axes of the system of symmetric dumbbells with an aspect ratio of $L^* = 0.2$ at a packing fraction of $\phi_{\alpha} = 0.550$ with applied shear rates of (a) $\dot{\gamma} = 0$ and (b) $\dot{\gamma} = 10$. An increase in peaks of the probability density suggests an increase in layering of particles perpendicular to the corresponding cartesian axis.

Figure 27 shows the probability density of the system along the cartesian axes of the simulation box for the dumbbell system with an aspect ratio of $L^* = 0.2$ at a packing fraction of $\phi_{\alpha} = 0.550$, with both the highest rate and with no rate of shear flow applied to the system.

$$P_{\alpha} = \frac{1}{N_p} \left\langle \sum_{i=1}^{N_p} \sum_{j>i}^{N_p} \delta(r - (r_{i,\alpha} - r_{j,\alpha})) \right\rangle$$
(60)

The probability density, P_{α} , is calculated by finding the distance between a reference particle $(r_i, i = 1)$ and every other particle in the system $(r_j, j > i)$ and breaking those distances down into the three separate cartesian axes of the simulation box, denoted by α . By averaging these distances over all particles, N_p , and a number of configurations along the simulation trajectory, we obtain the density of particles along the planes of the simulation box where the integral of the curve would be equal to unity. If the system was a perfectly dispersed fluid the probability density would show a linear line holding the P_{α} value of the inverse of the edge length of the simulation box. When $\alpha = x$ we are observing the probability density of particles in the yz plane along the simulation box, when $\alpha = y$ the xz plane, and when $\alpha = z$ the xy plane.

Figure 27a shows the system at equilibrium with peaks and troughs that imply some level of layering, however, all three axes are equivalent in layering implying an isotropic layering behaviour. Figure 27b shows the system under the highest rate of shear applied in this study of $\dot{\gamma} = 10$. Under a high shear flow, we observe that the layering in the x and z axes stay the same as in equilibrium yet the layering in the y axis noticeably increases. This implies the layering of dumbbell particles in the xz plane is increasing as the shear rate applied to the system is increased.

It was hypothesised by Wagner and Brady [22] that the shear thinning behaviour of hard sphere colloidal systems is due to the particles forming layers orthogonal to the shear-gradient direction (i.e. layering in the xz plane). The particles forming these channels reduce the collisions experienced by the particles under increasing shear rate, resulting in a decreasing shear viscosity and therefore a shear thinning behaviour. This layering behaviour is exactly what is observed in Figure 27 and is corroborated by the microstructure observed from the RDF data.

In a Stokesian dynamics simulation study of suspensions of hard sphere colloidal particles under shear by Xu *et al.* [23], layering and shear thinning were, in actuality, observed to be decoupled; instead contact particle pairs were found to align when projected on the flow-gradient plane. This alignment of the particles was thought to be the cause of shear thinning with the layering being coincidental as opposed to causal. The particle pair mentioned in the literature could be defined as a single dumbbell particle with the alignment of the pair of spheres being synonymous to the alignment along the symmetry axis of the dumbbell particle. According to the Jeffrey orbitals of prolate axisymmetric particles observed in the literature, it would be expected for the symmetric dumbbell particle to begin to align in the direction of shear flow at higher shear rates [55, 60].



Figure 28: Number of the symmetric dumbbell particles that align in the direction of shear flow, N_{align} , within a margin of 30° at varying aspect ratio as a function of $\log(\dot{\gamma})$. The data shown here is for the system at a packing fraction of $\phi_{\alpha} = 0.550$. with the number of aligned particles, N_{align} , being normalised by the number of particles in the system, N.

Figure 28 shows the average number of particles in the system that are aligned with the direction of shear flow, i.e. the x axis, as the shear rate is increased. These numbers were obtained by calculating the angle between the symmetry axis of the dumbbell particle and the x axis of the simulation box, allowing for a margin of 30° to be counted as aligned. The data shows a clear increase in alignment of the particles along the shear flow direction as the rate of shear is increased. However, the behaviour is reasonably weak

when considering that the system has 500 particles. The highest number of particles aligning in the flow direction observed in this system is only around a quarter of the total number of particles in the system. However, several studies have shown that the aligning behaviour of axisymmetric particles to the shear flow is maximally strong near the wall of the shearing implement, weakening to near-isotropic orientational behaviour towards the bulk of the flow channel [101–104]. The BD simulation utilised in this study is focused on the bulk behaviour of the system and may explain the present yet relatively weak alignment to the shear flow.

Despite the weakness in the alignment, the data correlates well with the shear thinning behaviour observed in the system. The highest aspect ratio dumbbell system, $L^* = 0.8$, has both the greatest aligning behaviour and the strongest shear thinning behaviour. The rate of shear thinning in the $L^* = 0.2$ and 0.5 systems are similar, reflecting the similar rate of growth in the number of particles aligning with the shear flow. However, the shear thinning behaviour appears to be fractionally stronger in the $L^* = 0.2$ system compared to 0.5, which contradicts the fractionally higher increase in alignment in the $L^* = 0.5$ system compared to 0.2. This may suggest some interplay between other properties of the system under shear.

Figure 29 shows that, in conjunction with the evidence of particle alignment with the shear flow, there is a clear increase in the rotational diffusion coefficient of the system as the shear rate is increased. The increase in rotational diffusion appears to be identical from a shear rate of $\dot{\gamma} = 0.1$ to 1 at all three aspect ratios. However, between the shear rates of $\dot{\gamma} = 1$ and 10 there is a greater rate of increase in the $L^* = 0.2$ opposed to the comparable increases for the higher two aspect ratio dumbbell systems. The increased



Figure 29: Plot of rotational diffusion coefficients of the symmetric dumbbell particles at varying aspect ratio as a function of $\log(\dot{\gamma})$. The data shown here is for the system at a packing fraction of $\phi_{\alpha} = 0.550$.

rotational diffusion in the low aspect ratio regime would be expected for the same reasons as in the equilibrium state, where there is less hindrance to tumbling rotations for the lower aspect ratio dumbbell particles. It can be hypothesised that the higher rotational diffusion observed under shear in the $L^* = 0.2$ system results in the fractionally stronger shear thinning behaviour compared to the system at an aspect ratio of 0.5. The rotation of the particles clearly play a role in the rheological behaviour of the system, but it is apparent that the microstructural behaviour of the alignment of particles with the shear flow is a more defining feature effecting the shear thinning behaviour of the symmetric dumbbell system.

3.3. Conclusions

A Brownian Dynamics simulation study was performed for a system of symmetric colloidal dumbbells to investigate the effects of shape anisotropy on the rheological behaviour of the system. The phase space was chosen such that the system would remain in the fluid phase at equilibrium to allow for effects of the shape anisotropy to be observed without the influences of a phase boundary. An intriguing non-monotonic dependence on the aspect ratio was observed in the translational diffusion and shear viscosity of the system. The competition between the density correlation and excluded volume was hypothesised to be the reasoning behind the non-monotonic behaviour. Stronger correlations, due to enhanced density correlation, dominated at smaller elongation, whereas slow decorrelations, due to increased excluded volume, dominated at larger elongation.

There also appears to be manifestations of translation-rotation decoupling in the system when comparing the non-monotonic behaviour of the translational diffusion and the monotonic behaviour of the rotational diffusion. This decoupling is as of yet still unresolved, it would be of great interest to discern the origin of this decoupling behaviour in future.

An external shear flow was then applied to the system to investigate how the elongation of the colloidal dumbbell particles may effect the dynamic response. The non-monotonic behaviour seen at equilibrium survived even the highest shear rates. A general shear thinning trend was observed at all aspect ratios, with the shear thinning being strongest in the highest aspect ratio system. Increased layering and alignment were observed in the system as the shear rate was increased. The literature suggests that layering proves to be coincidental opposed to causal in the hard sphere regime with shear thinning behaviour instead being driven by alignment. The trend in alignment match well with the shear thinning trends.

It was seen that the rotational behaviour of the system is somewhat important to the rheological behaviour of the system, but is overshadowed by the effect of the alignment of particles to the shear flow. It is very important to note that the BD simulation is an implicit solvent technique and does not take the hydrodynamic behaviour of the system into account. The inclusion of hydrodynamic behaviour in the system will be pivotal in fully understanding the rheological properties of a colloidal system due to the vast differences in timescales for solvent and colloid interactions.

4. EXPLORING THE EFFECTS OF CONTROLLED CLUSTER FORMATION ON THE RHEOLOGICAL BEHAVIOUR OF COLLOIDAL SUSPENSIONS

4.1. Introduction

Understanding the rheology of colloidal suspensions is key in the development of many products in the consumer goods industry, including food, cleaning products, adhesives and paints [6, 105]. Understanding rheological behaviour is vital to optimise production and transport of the product as well as improving the product itself. It is also important to probe how an external shear flow might disable, or enable, the aggregation of colloidal particles into many interesting applications, such as optical crystals, drug delivery systems and oil recovery [7–9].

It is widely recognised that the microstructure influences the rheology of a colloidal system [22]. However, it is still not well understood precisely how these structural changes affect the flow of the particles in the system or indeed how flow can affect the microstructure. It is equally important to understand how to control the microstructure of the system as well as how the microstructure can influence the rheology.

The focus of colloid rheology in the literature has largely been on dispersions of spherical colloidal particles with isotropic interparticle interactions [22, 29]. The spherical regime is well studied but is also limited to fairly simple microstructural behaviour. It has been shown by Leal and Hinch [53] that even a small deviation from the isotropic spherical shape can have a powerful effect on the microstructural and rheological behaviour of a system.

Recent advances in particle synthesis have made a variety of anisotropic colloidal particles available. These particles are anisotropic often due to shape and/or surface chemistry. Anisotropic colloidal particles are easily tuned to allow for a precise control on the interparticle interactions, which leads to control over the microstructure of the system [79].

Colloidal dumbbells offer an attractive model system to advance our understanding of how the microstructure governs the viscoelastic response of colloidal dispersions in the presence of anisotropic interparticle interactions. A colloidal dumbbell is able to encompass many forms of anisotropy to produce particularly interesting phase behaviour and microstrutures. Not only is a dumbbell axis-symmetric, introducing a variety of interesting orientational properties such as plastic crystals and aperiodic crystals [68, 69], but an asymmetry between the two lobes can be introduced to further diversify the phase diagram [106, 107].

Patchy colloids have been studied outside of the dumbbell particle shape, where clusters are able to be self-assembled for spherical repulsive particles with attractive patches at each pole [108]. Peng *et al.* [109] have shown both experimentally and theoretically that colloidal dumbbells can be used for self-assembly, or clustering of particles to achieve control in microstructure. Avvisati *et al.* [110] studied a patchy colloidal dumbbell system where one lobe was attractive and the other repulsive, demonstrating the formation of vesicle, micelle and bilayer structures using Monte Carlo simulations, as seen in Figure 30.

It is widely recognised that the microstructure influences the rheology of colloidal suspensions [22]. However, it is still not well understood precisely how these structural changes affect the flow of the particles in colloidal suspensions or indeed how flow can affect the



Figure 30: Image taken from ref [110]. Each panel shows a different microstructure formed in a patchy colloidal dumbbell system with vesicles, micelles and bilayers.

microstructure. It is equally important to understand how to control the microstructure of the system as well as how the microstructure can influence the rheology.

Chakrabarti and coworkers have recently established design rules for hierarchical selfassembly pathways to yield a variety of colloidal open crystals, especially for their photonic applications [111, 112]. The bottom-up route exploits a hierarchy of interactions, encoded in triblock patchy particles having attractive patches on the poles across a charged middle band [113], to programme two-stage self-assembly pathways via *self-limiting* clusters. The formation of self-limiting clusters ensures that the first-stage of assembly results in small colloidal clusters of well-defined size and shape, i.e. colloidal molecules, which serve as monodisperse secondary building blocks in the second-stage of assembly to yield open crystals. This series of work suggests that a geometric criterion, satisfied by the width of the patches and the range of patch-patch interactions is crucial for the formation of self-limiting clusters in the first stage. In this context, our hypothesis was asymmetric colloidal dumbbells in the presence of a hierarchy of interactions between the lobes should provide an alternative route to self-limiting clusters, where the size ratio between the lobes can be tuned to satisfy the geometric criterion.

The aim of this study was to validate our hypothesis to yield self-limiting colloidal clusters from designer asymmetric colloidal dumbbells and investigate the rheological behaviour of the cluster fluid in the presence of controlled cluster formation. To this end, we considered asymmetric colloidal dumbbells, each comprising two touching spherical lobes of different sizes. The colloidal dumbbells are treat as rigid bodies interacting via site-site generalised Lennard-Jones potential as described previously. The shape asymmetry is governed by the size ratio of the lobes and the surface chemistry can be exploited to realise a hierarchy of interactions.

The phase diagrams of hard asymmetric dumbbells are reported in the literature, either for touching spheres with varying constituent sphere diameter ratios (also referred to as snowman-shaped particles) or for fixed constituent sphere diameter ratio of 0.5 [106, 107]. In the present study, we consider attractive interactions for asymmetric dumbbells, combing shape anisotropy with energy anisotropy, for which the phase behaviour has not been reported previously to the best of our knowledge.

4.2. Discussion

4.2.1. Designer colloidal dumbbells

We set out to test our hypothesis that asymmetric colloidal dumbbells can form selflimiting clusters when the shape asymmetry and surface chemistry are tuned. To this end, we first employed the basin-hopping global optimisation technique to predict the global minima of finite systems as the likely structures to be observed at low reduced temperatures, with an objective to identify the parameter space that can plausibly support tetrahedral clusters. For a given size of the finite system, five basin-hopping runs were carried out, starting from randomly generated configurations and performing 10 million basin-hopping steps for each run. A large number of steps were run to sufficiently increase the level of confidence in the putative global minima that we present here.

The shape asymmetry is controlled by changing the size ratio between the two spherical lobes of the dumbbell particle. We set $\sigma_{AA} = 1$, and varied the value of $\sigma_{BB} > 1$ controlling the size of the other spherical lobe, away from the limit of a symmetrical dumbbell, with $\sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB})$. In search of parameterisation that can support repeating tetrahedral units, we considered a hierarchy of interactions strengths, i.e. we set $\epsilon_{AA} = 1$, varied $\epsilon_{BB} < 1$, with $\epsilon_{AB} = \sqrt{\epsilon_{AA} \epsilon_{BB}}$. Such a choice of parameter set ensures that the smaller lobes of the asymmetric dumbbells interact favourably, governed by the surface chemistry, and probes the effects of decreasing the interaction strength of the bigger lobe.

By introducing a hierarchy of interaction strengths between the two lobes of the dumbbell, an energetic bias is formed towards the clustering of one lobe before secondary interactions



Figure 31: Putative global minima on the potential energy surface for finite systems of N = 4 (a) and N = 6 (b) asymmetric colloidal dumbbells with $\sigma_{AA} = 1$, $\sigma_{BB} = 5$, $\epsilon_{AA} = 1$ and $\epsilon_{BB} = 0.5$. The structures show the propensity for forming tetrahedral clusters, with an inner tetrahedral motif formed by the smaller lobes. In this snapshot representation, lobe A of the dumbbell is coloured red and lobe B grey. In (a), the large lobes of the asymmetric dumbbell particles have been kept to scale, however in (b), the large lobes have been scaled down to 80% to provide a better view on the smaller lobes.

between the second lobe occur. In conjunction with the interaction asymmetry, a shape asymmetry is introduced to form a steric barrier when enough dumbbells cluster together; limiting the cluster from growing any further. A balance of the two types of asymmetry are required to achieve self-limiting cluster formation.

Figure 31 shows the putative global minima on the potential energy surface for finite systems of N = 4 and N = 6 asymmetric colloidal dumbbells that we identified for $\sigma_{AA} = 1$, $\sigma_{BB} = 5$, $\epsilon_{AA} = 1$ and $\epsilon_{BB} = 0.5$. For N = 4, we see a tetrahedral cluster, where the smaller lobes interact with each other to pack in a tetrahedral motif, which is shielded by the larger lobes forming an outer tetrahedron. In the cases of N = 5 (not shown here) and N = 6 systems, the propensity to form a tetrahedral unit is apparent, with the remaining particle(s) attached to the tetrahedral unit. The hierarchy of interaction strengths is what enables the smaller lobes to cluster together preferentially, while an optimal size ratio is critical to satisfying the geometric criterion that limits the number of smaller lobes facing inward.

Next we considered a bigger finite system with N = 12 asymmetric colloidal dumbbells and investigated the effects of the shape asymmetry on the morphology of the system by varying σ_{BB} from 5, while keeping the hierarchy of interactions intact, i.e. $\epsilon_{AA} = 1$ and $\epsilon_{BB} = 0.5$. Figure 32a shows the putative global minimum energy structure for a 12particle system consisting of three tetrahedral units. These units are clustered together for optimal interactions between the larger lobes. We narrowed down the parameter space that would give this structure as the global minimum to be between $\sigma_{BB} = 4.5$ and $\sigma_{BB} = 6.5$. The trend for forming tetrahedral units continues with the N = 16 system with the putative global minimum consisting of four tetrahedral units, as evident in Figure 32b.



(a) 12-particle system

(b) 16-particle system

Figure 32: Putative global minima on the potential energy surface for finite systems of N = 12 (a) and N = 16 (b) asymmetric colloidal dumbbells with $\sigma_{AA} = 1$, $\sigma_{BB} = 5$, $\epsilon_{AA} = 1$ and $\epsilon_{BB} = 0.5$. The propensity for forming tetrahedral units continues as the size of the finite system grows. In this snapshot representation, lobe A of the dumbbell is coloured red and lobe B grey. Here, the size of the larger lobes of the dumbbells is scaled down to offer a better view of the smaller lobes.

Unlike in the smaller systems, it was observed for the 12- and 16-particle systems that

the global minimum structure was found for all five basin-hopping runs starting from independent random configurations only in the range of σ_{BB} values between 5 and 5.5. Above a σ_{BB} value of 5.5 and below 5, not all of the 5 basin-hopping runs could find the global minimum structure even after 10 million simulation steps, indicating the existence of deep local minima that might be difficult to escape from to find the global minimum structure. The implication for this observation is that the structures that are desired are likely to be difficult to reach in the bulk dynamic simulations, let alone in experiments.

We chose to consider the $\sigma_{\rm BB}$ value of 5, concerning smaller shape anisotropy, for further investigation to assess the ratio of interaction strengths between $\epsilon_{\rm AA}$ and $\epsilon_{\rm BB}$, keeping the former fixed to unity. As $\epsilon_{\rm BB}$ was varied between 1 and 0.2 for a 12-particle system, the global minimum structure was found to consist of 3 tetrahedral units between 0.5 and 0.2. While a more pronounced hierarchy of interactions provides a stronger energetic driving force, a larger bias in the interaction interaction strengths could be more difficult to realise experimentally. We therefore decided to proceed with $\epsilon_{\rm BB} = 0.5$ and $\sigma_{\rm BB} = 5$ with $\epsilon_{\rm AA}$ and $\sigma_{\rm AA}$ set to unity for assessing the success of self-limiting cluster formation in Brownian Dynamics simulations of a system of N = 500 asymmetric colloidal dumbbells.

4.2.2. Bulk simulation at equilibrium

We carried out a Brownian Dynamics simulation of a 500 particle system of asymmetric dumbbells with a hierarchy of interaction strengths, interacting via a depletion interaction, which was modelled by the generalised Lennard-Jones potential. Optimised in the global optimisation simulations, the smaller lobe ($\sigma_{AA} = 1$) has a greater interaction strength ($\epsilon_{AA} = 1$) compared to the larger lobe ($\sigma_{BB} = 5, \epsilon_{BB} = 0.5$). Unlike in the global optimisation study, the bulk dynamic simulations are temperature-dependent resulting in the necessity for the system to be slowly annealed in order to facilitate the formation of clusters. The annealing process consisted of bringing the system to equilibrium, lowering the temperature and then running the simulation until reaching a steady state at the new temperature. We would expect to then repeat this process until we observe the end of a phase transition. We applied the annealing to a number of systems with varying packing fractions, ϕ , to ensure we sample a good portion of the phase space leading to the observation of the desired behaviour. We used packing fractions of $\phi = 0.18, 0.29$ and 0.39. We ran the system first at a reduced temperature, T^* , of 0.36, resulting in an equilibrium system in the liquid state. We then lowered the temperature by 0.02 down to $T^* = 0.30$, and further in increments of 0.01 down to $T^* = 0.15$.



Figure 33: The left y-axis shows the number of individual tetramers formed from 4 dumbbells coming together with the smaller lobes facing inward as we annealed the system. The right y-axis shows the average energy per particle as we annealed the system.

Figure 33 shows the growth of tetramer clusters formed in the system along the annealing

trajectory. The non-linear change in the average energy per particle matching with the growth of tetramer clusters beginning from a temperature of 0.30, shows that the system is undergoing a phase transition as it is annealed. By the end of the annealing process, just over 100 tetramer clusters were formed, translating to over 80% of particles in the system being a part of a tetramer cluster. We do not see 100% of the system forming tetramer clusters as at a low enough temperature the secondary interactions of the large lobes become strong enough to not be broken under thermal fluctuations. The formation of these secondary bonds cause the dumbbell particles, not already forming tetramer clusters, to be unable to move into the correct position and orientation to form the primary bonds needed for the formation of the tetramer clusters.

Note here that we are referring to tetramer clusters and not the regular tetrahedra that were predicted in the global optimisation simulations. To call a cluster a regular tetrahedron, a cluster of four dumbbell particles is identified, for which an orientational tetrahedral order parameter, q, is calculated to determine the regularity of the tetramer cluster [114, 115].

$$q = 1 - \frac{3}{8} \sum_{a=1}^{3} \sum_{b=a+1}^{4} \left[\cos(\theta_{ab}) + \frac{1}{3} \right]^2$$
(61)

where θ_{ab} is the angle between the axes of symmetry of two dumbbell particles, denoted as a and b, in the 4-particle cluster. The value of q ranges from 0 for an isotropic orientation up to 1 for the perfect orientation for a regular tetrahedron and is commonly used to quantify the local structure of water in various conditions [115–117].

As described above, a q value of 1 requires perfect orientations of the dumbbell particles which would be unrealistic to expect in a dynamic system. A cut-off value was utilised in the order parameter calculation to allow for some slight deviations in otherwise regular tetrahedra. When running the order parameter with a cut-off of 0.99, it was seen that only around 70% of the tetramer clusters were classed as regular tetrahedra. However, when the cut-off was relaxed to 0.95, where the shape of the cluster still closely resembles a tetrahedron, over 95% of the tetramer clusters were counted as regular tetrahedra. This indicates that the vast majority of tetramers in the system are effectively regular tetrahedra with some minor deviations in orientations due to the temperature-dependent nature of the simulation. Mathematically perfect tetrahedra would be an unrealistic means of assessing the cluster formation in the system. The rest of this study will refer to tetramer clusters and not regular tetrahedra when reporting cluster analysis.



Figure 34: Radial distribution functions for a range of reduced temperatures along the annealing trajectory for the $\phi = 0.18$ system. The distance r is given in the reduced unit of length. In the case of the asymmetric dumbbell, the reduced unit of length is set to σ_{AA} .

Figure 34 shows the radial distribution functions (RDF) of the lowest density system at various points along the annealing trajectory. The range of reduced temperatures were chosen as they represent the system at key stages in tetramer cluster formation. At a reduced temperature of $T^* = 0.36$ the system is in an equilibrium fluid state with no tetramer cluster formation. The reduced temperatures of $T^* = 0.25, 23$, and 0.20 are points along the annealing trajectory where 25, 50, and 75% of the particles in the system made up the tetramer clusters, respectively. It is apparent that there is an increase in translational order in the system as the temperature is lowered. The first peak in the distribution function corresponds to the distance between the centre-of-mass of a dumbbell particle and that of a neighbouring particle at contact. The increase in the size of the first peak indicates the growth of contact neighbours corresponding to the growth of clusters. The increase in the height of peaks at roughly 8.9σ and 10.3σ indicate the growth of tetramer clusters, specifically, as they correspond to the distance between an asymmetric dumbbell and dumbbells of a neighbouring tetramer cluster.

As apparent from Figure 34, g(r) at $T^* = 0.20$ shows more features at larger separation, indicating a non-trivial microstructure. The emergence of this microstructure at the lowest temperature studied suggests that the weaker interactions at play, involving the larger lobe of the dumbbells (i.e. A-B or B-B interactions), have begun to form longer lasting bonds. At higher temperatures, the life times of the A-B or B-B bonds are small enough to facilitate the formation of tetramers (largely tetrahedral clusters), which grow in number as the temperature is lowered. With around 80% of the dumbbells forming tetramers at $T^* = 0.20$, the smaller lobes are still exposed to form A-B bonds. The longer lifetimes of these A-B bonds disrupt the formation of tetramers and connect clusters together; leading to the non-trivial microstructure quantitatively observed in the RDF data. However, visual inspection confirms the lack of long-range crystalline order in the system at this temperature.



Figure 35: Growth of clusters in the $\phi = 0.18$ system. Each size of cluster is given on the graph as a % of the 500 particles in the system that make up all the clusters in the system. The x-axis represents the trajectory of time over the annealing simulation; it has non-significant units and have been removed for ease of viewing.

Figure 35 shows the growth of clusters in the $\phi = 0.18$ system over the annealing process. To measure the growth of clusters in a system, we employed a graph theoretical method using the depth-first search algorithm to establish the number of connected particles in each cluster of the system. The system structure is represented as a graph of vertices where each vertex represents a particle. Edges are created between vertices if the distance between two particles are within a cut-off parameter. The depth-first search algorithm then searches the whole structure for connected particles and calculates the size of every cluster in the system.

The annealing was started from the equilibrium fluid state of the system where around 95% of the dumbbells in the system were monomers with a small percentage making up dimer clusters. As the annealing process starts, there is a sharp drop in monomers as the smaller lobes of the asymmetric dumbbells begin to interact to form larger clusters. It

is clear from the early stages of the annealing process that the dumbbells form smaller clusters before tetramer clusters begin to form. This is further reinforced as we continue along the trajectory, where we see the growth of dimers and trimers are stunted as the tetramer clusters are formed, suggesting that dimers and trimers are the pathway to growing the tetramer clusters. Eventually the % of dumbbells that form the trimer clusters level off completely, implying that the dumbbells are forming trimers at the same rate as the trimers are interacting with monomers to form tetramer clusters. The continuous decline in the % of dumbbells forming dimers could suggest that the dimers are both interacting with monomers to form trimers, and also interacting with other dimers to form directly into tetramer clusters. As there are two paths to dimer loss we observe a faster rate of dimer loss than growth and therefore a decline in dimer clusters along the annealing process. These observations suggest that there are multiple pathways to form tetramer clusters. As each temperature in the annealing process is continued until an steady state is reached, it is apparent that the system does not require every monomer to form intermediate clusters before continuing to form tetramers. Most importantly, there is no indication of the formation of larger clusters than the tetramers as the system is annealed, strongly supporting the success of the design principle to achieve self-limiting cluster formation.

The shear viscosity, η_{eq}^* , at equilibrium was calculated using the Green-Kubo relation of the stress auto-correlation function. Figure 36 shows the equilibrium viscosity as a function of temperature for all three systems of varying packing fractions. A small, steady increase in η_{eq}^* was observed as the temperature of the system was lowered. A general upward trend in η_{eq}^* as temperature decreases is expected, regardless of microstructural change, as the dumbbells would have less kinetic energy. However, the increase correlates well with the



Figure 36: The equilibrium viscosity of the system along the annealing trajectory. Each of the three systems with packing fractions $\phi = 0.18, 0.29$ and 0.39 have been reported. Error bars are included from three independent simulations. NOTE: The data point for $\phi = 0.39$, $T^* = 0.20$ is missing error bars. The calculation of equilibrium viscosity becomes unreliable at low temperatures due to kinetic arrest.

increase in cluster formation and there is a sharp increase in η_{eq}^* as we approach the peak count of tetramer clusters. We expect to observe the viscosity of a system to increase as the number and size of clusters increase due to the reduced mobility experienced by "particles" with more mass (or in this case larger clusters compared to monomers). It is sound reason to believe that a larger particle (or cluster of particles) would also experience more drag from the solvent medium, however, the hydrodynamics of the system are not captured in this Brownian Dynamics framework and so this hypothesis cannot be drawn. Although the sharp increase in viscosity may reflect the sharp increase of tetramer clusters in the system, the RDF data showed that the system at low temperature is beginning to see increased long-range order from the secondary interactions between the larger lobes of the asymmetric dumbbells. This increase in long-range order may be the cause for the increasing viscosity.
An external shear was applied to the equilibrated states of the system at various points along the annealing simulation. The systems investigated were the equilibrated states at reduced temperatures of $T^* = 0.36, 0.25, 0.23$, and 0.20, at these points along the simulation trajectory 0, 25, 50, and 75% of the system made up the tetramer clusters, respectively. These systems were chosen for study in order to probe the effect of different levels of cluster formation on the rheological behaviour of the system.



Figure 37: Shear viscosity of the system against the logarithmic shear rate at a range of reduced temperatures from $T^* = 0.36$ to 0.20. (a), (b), and (c) are plots of systems at a packing fraction of $\phi = 0.18, 0.29$ and 0.39 respectively. Error bars are included from three independent simulations.

It can be seen in Figure 37 that every system exhibits shear thinning behaviour, where

the viscosity decreases with increasing shear rate. The shear thinning becomes more pronounced in denser systems and is much stronger for the systems at lower temperature. This stronger shear thinning behaviour at lower temperatures appear to indicate that the higher number of tetramer clusters in the system has a strong effect on the rheological behaviour of the system under shear. However, it appears that, as the shear rate is increased, the viscosity of the systems at all temperatures converge to the viscosity of the equilibrium liquid state of the highest temperature system, $T^* = 0.36$. The converging viscosities suggest that the systems may be reverting to the microstructure of the fluid state. This could mean the shear thinning behaviour may not be an effect driven by the presence of clusters in the system and instead purely the loss of these clusters as the system is driven back to the fluid state. Once converged, the viscosity continues to decrease, at a much lower gradient, as the shear rate is further increased. As the continued shear thinning is present in the highest temperature system, it is clear that the continued shear thinning is not an effect due to the presence of clusters in the system.



Figure 38: Radial distribution functions for the $\phi = 0.18$ system at a variety of shear rates from $\dot{\gamma} = 0.01$ to 10.0. (a) shows the system at a reduced temperature of $T^* = 0.23$, where the system has 50% of its particles in tetramer clusters. (b) shows the system at a reduced temperature of $T^* = 0.20$, where the system has 75% of its particles in tetramer clusters.

Figure 38 shows the RDF analysis of the lower temperature systems of packing fraction $\phi = 0.18$ under a range of applied shear rates. As the rate of shear applied to the system was increased the order, previously observed in the equilibrium state of the annealed system, was lost. Translational order is lost in every system under a shear rate of $\dot{\gamma} = 5.00$, with the higher temperature systems, although not shown here, losing order even under the application of a shear rate of $\dot{\gamma} = 1.00$. The RDF analysis corroborates the observation from the shear viscosity data that the system is converging to that of the fluid state.

Figure 38b shows that the advanced structural order, observed due to the secondary interactions between the large lobes at the lowest reduced temperature, survives the lowest shear rate. However, the order is lost beyond the lowest shear rate of $\dot{\gamma} = 0.01$, returning back to the translation order observed at the higher temperatures. Both panels in Figure 38 still show the peaks at roughly 8.9σ and 10.3σ at a shear rate of $\dot{\gamma} = 0.10$, which suggests that the clusters in the lower temperature systems are somewhat resistant to shear. However, the peaks are reduced in intensity at each increasing increment of shear rate, implying that the clusters are being broken down to some extent at every shear rate. The RDF analysis suggests that the far steeper shear thinning behaviour seen at the lowest temperature system is most likely due to the breaking of the secondary interactions and therefore the loss of the advanced structural order. The systems are all appearing to be returning to the fluid state in a continuous manner as a function of increasing shear rate, which may explain the rest of the shear thinning behaviour. The RDF does not shed light on the shear thinning behaviour beyond the convergence of shear viscosities to that of the fluid state.

In the cluster analysis, seen in Figure 39, it was clear that clusters were destroyed as the



Figure 39: Growth and loss of clusters due to different rates of applied steady shear, $\dot{\gamma}$, on the $\phi = 0.18$ system at a reduced temperature of $T^* = 0.23$. Each size of cluster is given on the graph as a % of the 500 particles in the system that make up all the clusters in the system. The x-axis represents the trajectory of time over the annealing simulation; it has non-significant units and have been removed for ease of viewing.

shear rate applied to the system was increased. In the $\phi = 0.18$ system at a reduced temperature of $T^* = 0.23$, the tetramer clusters were all but completely lost at a shear rate of $\dot{\gamma} = 1.00$. When a shear rate of $\dot{\gamma} = 10.0$ was applied to the system, not only were the tetramer clusters destroyed, but the trimer clusters had also broken apart. Although the clusters were all but lost when high shear rates were applied to the system, it was also observed that the % of particles in each cluster size were only slightly reduced at the lower shear rates. These observations corroborate the data seen in the RDF analysis. Only the cluster analysis of one system is shown here for multiple shear rates, however, the same general trends were seen at all packing fractions and temperature systems. Systems with more tetramer clusters at equilibrium, i.e. lower temperatures, withstood a slightly higher shear rate before complete collapse of the clusters into dimers and monomers. This was most likely due to the shear flow needing to breakdown the secondary interactions between the larger lobes of the asymmetric dumbbells before the clusters were affected.

From the RDF and cluster analysis it is clear that the system is reverting back to the fluid state under increased rates of shear. It appears that the shear thinning behaviour at lower shear rates observed in our simulations were all down to the breaking up of the clusters. The loss of clusters was an unintended result and most likely down to the relatively weak interactions between the colloidal dumbbell particles. We would need to see a wider range of shear rates in which the clusters remain stable in the system so that we can properly analyse the effect of cluster formation on the rheological properties of the system under shear. An annealing of an asymmetric dumbbell with stronger interactions would be of interest in future in order to complete the investigation on the rheology of the system as a function of cluster formation.

Figure 40 shows the alignment of the symmetry axis of the dumbbells with the direction of shear flow increasing as the rate of shear applied to the system is increased. The alignment with the flow direction was measured with a margin of 30° with almost half of the dumbbells in the system aligning at the highest shear rate. It has been shown in the literature, that the shear thinning behaviour of hard axisymmetric particles can be attributed to the alignment along the direction of shear flow [55, 60]. Although the literature studies were conducted on prolate particles with a much higher elongation than in the case of our asymmetric dumbbell particles, the hierarchy of the interactions along the axis of symmetry may be promoting the bias towards aligning with the shear flow. The alignment of particles is most likely the cause of the shear thinning behaviour of the fluid state.



Figure 40: Number of the dumbbell particles that align in the direction of shear flow within a margin of 30° at varying points along the annealing trajectory as a function of $\log(\dot{\gamma})$. The data shown here is for the system at a packing fraction of $\phi = 0.29$.

4.3. Conclusions

In this chapter, we have validated our hypothesis that designer asymmetric colloidal dumbbells can form self-limiting clusters, by exploiting the size ratio between the lobes and a hierarchy of interaction strengths between them. A global optimisation study of finite systems was conducted for asymmetric colloidal dumbbells to determine the parameter space that would support structures with repeating tetrahedral units. This study led us to a set of parameters for Brownian Dynamics simulations under periodic boundary conditions. Our Brownian Dynamics simulations establish the design principles for the asymmetric colloidal dumbbells to form self-limiting clusters. Upon gradually cooling, we find a growth in the fraction of particles forming self-limiting tetrahedral clusters, with roughly 80% of them forming tetrahedral clusters at the lowest temperature studied. 100%cluster formation was not observed due to the secondary interactions of the weaker lobes, which had begun to kinetically trap the dumbbell particles not already in tetrahedral clusters from rearranging to form new tetrahedral clusters. The cluster analysis shows that smaller dimers and trimers are formed first and the tetramers are formed through multiple pathways from these smaller clusters and monomers. No larger clusters were observed, implying that the chosen set of parameters is robust for self-limiting cluster formation.

The increase of clusters in the system was mirrored in the increase of equilibrium shear viscosity. It is important to note that the trend in viscosity is also reflecting the decreasing in system temperature to some extent. The drastic increase in viscosity at the lowest temperature system is most likely down to the secondary interactions starting to come into play.

An external shear flow was then applied to the system to investigate the response in the presence of self-limiting clusters. A strong shear thinning behaviour was observed with the viscosity of all systems converging to the fluid state viscosity. The microstructural data showed that the clusters were breaking apart as higher shear rates were applied to the system, bring the system back to the microstructural state of the fluid system. The clusters were most likely breaking apart as the interactions holding the clusters together were not strong enough to withstand the shear flow. It would be of importance to investigate the annealing of a system of asymmetric dumbbell particles with higher interaction strengths as the effect of the presence of clusters on the rheological response of the system due to an external shear flow is yet to be answered. The shear thinning behaviour that continues in the fluid state corresponded to the alignment of particles with the direction of shear flow, as expected from the literature.

5. INVESTIGATING THE EFFECT OF SHAPE ANISOTROPY ON THE MICROSTRUCTURE OF TEMPERATURE QUENCHED COLLOIDAL SYSTEMS

5.1. Introduction

Colloidal gels, typically characterised by a space-spanning network of colloidal particles, are commonly encountered in our everyday life in foods and cosmetics. Gelation has been studied extensively for spherical colloids with attractive interactions [42, 118], and to a significantly lesser extent for shape-anisotropic colloidal particles [119–121]. For spherical colloidal particles with isotropic, short-range attractions, it has been observed that gelation is caused by arrested phase separation initiated by spinodal decomposition [118]. However, for shape-anisotropic colloidal particles, there may even be an alternative "nonsticky" route to gelation with a shift from the common paradigm, as revealed in a very recent study [122]. Such a revelation calls for more extensive investigation of gelation for shape-anisotropic colloidal particles.

The full understanding of the properties of the gel regime alongside the mechanism for gelation itself is still disputed in the literature [118, 123]. A colloidal gel can be difficult to characterise and is very similar in physical properties to the colloidal glass [124]. A colloidal glass is generally observed when repulsive interactions are involved, however, attractive glasses are also observed at high packing fraction. The separating definition of a colloidal gel is that it is observed from attractive interactions at low packing fractions [118, 124].

A plausible route to a non-equilibrium gel is quenching, i.e. reducing the temperature. A quench, often carried out instantaneously, into a two-phase region may lead to a dynamic arrest [42]. Royall and Malins [123] discussed the role of quench rate in colloidal gels in a system of spherical colloids with a relatively short-ranged attraction, in which the equilibrium state is gas-crystal phase coexistence. As reported in their Brownian Dynamics study, controlled quenching results in an enhancement in the degree of local order in the resulting gel, while local crystallisation is found for sufficiently slow quenching [123]. The rapid cooling makes it difficult for the system to properly nucleate into a crystal structure, which is commonly a slow process [125]. The much faster process of random local ordering in the system frustrates the nucleation of the crystal where the system can then kinetically arrest into a gel structure.

The non-crystalline states may therefore arise from frustrations in the nucleation process due to rapid quenching favouring random local ordering. By utilising the shape anisotropy of colloidal dumbbell particles, it may be possible to introduce a bias towards different local ordering in the system; therefore, affecting the frustrations leading to the interesting arrested states. The aim of this computational study is to investigate the effects of shape anisotropy on the microstructures formed in a system of symmetric colloidal dumbbells with short-ranged attractions upon quenching.

5.2. Discussion

5.2.1. Quenching the system

A Brownian Dynamics simulation was conducted on a system of symmetric colloidal dumbbells modelled using the generalised Lennard-Jones potential with an exponent of n = 24. A 500 particle system of symmetric dumbbells were studied over a range of aspect ratios, or dumbbell elongation, from $L^* = 0.2$ to 0.8 at an effective packing fraction of $\phi_{\alpha} = 0.1$. Each aspect ratio system was initially simulated at a high reduced temperature of $T^* = 2.0$ until an equilibrium state was reached. The reduced temperature of each system was then instantaneously dropped to $T^* = 0.3$ in order to simulate a temperature quench. The simulations were run for 200 million steps at a reduced timestep of $\Delta t =$ $2.5 \times 10^{-6}\tau$ to reach a steady state. The system parameters and quench protocol were chosen through reviewing work by Lodge and Heyes [126] who studied the quenching of spherical particles using the same potential model. The study reported "transient colloidal gels" with gel-like physical properties in the system after the temperature quench.

Figure 41a shows the radial distribution function (RDF) data for the lower aspect ratio systems of $L^* = 0.2$ and 0.4 at the quenched steady state. It can be observed that the systems have moved away from the fluid phase and some long-range local order has manifested. The first three peaks of these RDF plots correspond to a pair of neighbouring dumbbells in side-by-side, 'T' and end-to-end configurations respectively, as discussed in chapter 3. The first peak of both the $L^* = 0.2$ and 0.4 systems have very high intensity suggesting the presence of some strong orientational order in the system towards the parallel configuration. Unlike for the second and third peaks, which differ in range as a



Figure 41: Radial distribution functions for the centres of mass of the symmetric colloidal dumbbells for a range of aspect ratio L^* values, obtained upon quenching from $T^* = 2$ to $T^* = 0.3$ at the effective packing fraction $\phi_{\alpha} = 0.1$.

function of aspect ratio, the long-range order in the RDF data show coinciding peaks in both systems. This suggests there is some long-range behaviour invariant to aspect ratio. The peak positions themselves imply the presence of a hexagonal close-packed structure indicating crystalline behaviour in the system opposed to the gel-like structures that were reported in the spherical regime [126].

An interesting feature in the RDF plots of the higher aspect ratio systems is the peak below r = 1. As the RDF is calculated using the centre-of-mass of the dumbbell particles, this corresponds to two symmetric dumbbell particles in an 'X' configuration. When in the 'X' configuration, the centre-of-masses of two dumbbells can be closer than the diameter of lobe due to the free space between the two lobes. At higher aspect ratios, the elongation is such that there is more space between the two lobes of a dumbbell resulting in smaller distance for the peak. The affinity to the 'X' configuration of dumbbells does not necessarily suggest less orientational order, however, in conjunction with the rest of the RDF plot for the high aspect ratio systems the structures appear to be more frustrated than the low aspect ratio regime.

L^*	D_{COM}	D_{\perp}	D_{\parallel}
0.2	0.0065	0.0064	0.0067
0.4	0.0084	0.0082	0.0088
0.6	0.0103	0.0102	0.0104
0.8	0.0134	0.0131	0.0140

Table III: Translational diffusion coefficients for the centre-of-mass (COM), perpendicular (\perp), and parallel (||) translations of the symmetric dumbbell particles at varying elongations after a temperature quench down to $T^* = 0.3$.

Table III shows the translational diffusion coefficients of the quenched states over the range of aspect ratios giving information on the dynamics of the systems. The diffusion coefficients appear to show that the system is under kinetic arrest at all aspect ratios. There appears to be a trend of increasing translational diffusion as the aspect ratio of the dumbbell is increased, however, it is hard to elucidate the reason for this trend beyond the simple observation that the translational order is inversely proportional to the trend in diffusion. In any case, the values are all minute and effectively indicate a lack of translational movement in the system at the low temperature.

Figure 42 shows snapshots of the simulations of the quenched steady states of varying aspect ratio at a system density of $\phi_{\alpha} = 0.1$. The snapshots show what appear to be spacespanning structures at every aspect ratio. The higher two aspect ratio systems, $L^* = 0.6$ and 0.8, in particular, show gel-like structures. It is important to note here that structures of this kind can be prone to finite-size effects; as the system size is fairly small with only 500 dumbbell particles, the periodic simulation box is small and may be incorrectly suggesting that the amorphous structure is a space-spanning network, opposed to simply a large cluster of particles reaching the edges of the box. Simulations of larger systems should be investigated to eliminate this possibility, however, due to time constraints this could not be completed for this body of work. By visual inspection, there appears to



Figure 42: Snapshots of representative configurations of the systems of symmetric colloidal dumbbells for different values of the aspect ratio L^* at the steady state at $T^* = 0.3$ following the temperature quench at the packing fraction $\phi_{\alpha} = 0.1$. NOTE: The dotted lines are purely a visual aid and is not a direct reflection of the simulation box.

be an increased orientational order in the lower two aspect ratio systems, $L^* = 0.2$ and 0.4. These systems have formed hexagonal close-packed sheets of particles with dumbbells in parallel orientation with regards to the principle axes of elongation. The orientation of the dumbbells in the plane corroborate the observations seen in the RDF analysis. As the dumbbells are in parallel orientation there would be no change in the centre-of-

mass distance between neighbouring particles as a function of aspect ratio, leading to the coinciding peaks seen in the Figure 41a. Important to take note here that although the hexagonal close-packed sheets show an increase in local order there is no "global" order in the system with the sheets attaching to each other in seemingly random orientations in space.

As the aspect ratio is increased, the planar structures are lost with an amorphous structure taking its place; mirrored by the loss of long-range order in the RDF analysis of the higher aspect ratio systems.

Figure 43 shows the orientational distribution function (ODF) data for the quenched systems at steady state. The local orientational order in these systems can be used to quantify the trend in order observed by eye in the snapshots of the simulations. The ODF is calculated using the second Legendre polynomial, $P_2(cos\theta_{ij})$,

$$P_2(\cos\theta_{ij}) = \frac{1}{2}(3\cos^2\theta_{ij} - 1)$$
(62)

where θ_{ij} is the angle between the principle axes of elongation between the particle pair. $P_2(\cos\theta_{ij})$ holds a value of 1 when two dumbbells are in a parallel configuration and a value of -0.5 for a perpendicular configuration. A probability function, $gP_2(r)$, is then calculated which measures the probability of the orientation of particles at a particular distance from a reference particle.

$$gP_2(r) = \frac{1}{\rho N_p} \left\langle \sum_{i=1}^{N_p} \sum_{j>i}^{N_p} P_2(\cos \theta_{ij}) \delta(r - (r_i - r_j)) \right\rangle$$
(63)

The function, $gP_2(r)$, takes the sum of $P_2(\cos \theta_{ij})$ values for particles at a distance r from

a reference particle averaged over all configurations and particles.

Figure 43a clearly shows a strong trend of orientational order at the lower aspect ratios. Further to this, the ODF data clearly shows large positive peaks at r = 1, confirming that there is a strong bias towards parallel orientation of the dumbbell particles in the lower aspect ratios. Figure 43b shows the higher aspect ratios exhibiting a deep trough at a pair distance below σ which corroborates the observation in the RDF suggesting that the local order of the dumbbells are dominated by perpendicular interactions forming pairs in an 'X' configuration.



Figure 43: Orientational pair distribution functions for the symmetric colloidal dumbbells for a range of aspect ratio L^* values, obtained upon quenching from $T^* = 2$ to $T^* = 0.3$ at the effective packing fraction $\phi_{\alpha} = 0.1$.

In all configurations there are four interactions occurring between dumbbell pairs; the two lobes of a dumbbell interacting with the adjacent lobes of the other dumbbell (AA and BB interactions) and then the lobes interacting with the diagonally opposite lobe of the other dumbbell (AB and BA interactions). In the 'X' configurations all of these interactions are equivalent. However, in the parallel side-by-side configuration, the AA and BB interactions differ from the diagonal AB and BA interactions. The AA and BB interactions are equivalent to each other and are interacting at the optimal distance for the potential, which for the generalised Lennard-Jones potential with an exponent of n = 24is 1.02σ . The diagonal AB and BA interactions are also equivalent to each other with an interaction distance of $\sqrt{(AA)^2 + (L^*)^2}$, demonstrating a steep increase as a function of aspect ratio equating to distances of 1.04σ , 1.10σ , 1.18σ , and 1.30σ for $L^* = 0.2, 0.4, 0.6$, and 0.8 respectively.

For the potential utilised here, two lobes at a distance of 1.02σ experiences 100% of the potential energy. In turn, a distance of 1.04σ experiences over 95%, 1.10σ experiences around 40%, 1.18σ experiences under 10%, and finally, 1.30σ experiences less than 1% of the potential energy. The range of the potential limits the viability for the parallel configuration of symmetric dumbbells, with the configuration becoming unsustainable as the symmetric dumbbell is elongated. It is our hypothesis that this geometric constraint is what drives the observations made in the microstructural behaviour of the quenched steady states as a function of aspect ratio. With the low aspect ratio regime forming randomly ordered hexagonal close-packed sheets with parallel orientations of dumbbells within the sheets, and the high aspect ratio regime forming more frustrated amorphous-like structures.

Global optimisation studies were conducted for the system to ascertain the optimal energetic behaviour of the system as a function of aspect ratio and therefore provide evidence for our hypothesis. As a temperature-independent study, the global optimisation data provides information on the energetic reasoning for the behaviour observed regardless of the temperature of the system. Figure 44 shows the global minimum configurations of the 2-particle systems at every aspect ratio under study. As expected, the optimal lowest energy configuration is the 'X' configuration allowing every lobe to interact with both



Figure 44: Configurations corresponding to the global minima on the potential energy surface for the 2-particle systems of symmetric colloidal dumbbells for different values of the aspect ratio L^* .

lobes of the neighbouring dumbbell at the optimal distance for the potential.

Figure 45 shows the global minimum configurations of the 8-particle system. Compared to the 2-particle system, there is a clear difference in the global minimum energy structures observed as a function of aspect ratio. The lowest aspect ratio system, $L^* = 0.2$, shows the hexagonal close-packed sheet structure with the dumbbells oriented in parallel with respect to the axis of symmetry. The planar structure is regular at the lowest aspect ratio and becomes more frustrated with the gradual re-appearance of the 2-particle global minimum 'X' configuration as the aspect ratio increases. At an aspect ratio of $L^* = 0.8$ the structure is formed solely of several 'X' configuration dumbbell pairs interacting with neighbouring pairs.



Figure 45: Configurations corresponding to the global minima on the potential energy surface for the 8-particle systems of symmetric colloidal dumbbells for different values of the aspect ratio L^* .

Although the 'X' configuration is the most stable 2-particle structure, this configuration is hindered in the multi-particle regime as it does not pack efficiently. The lack of efficiency is exacerbated at lower aspect ratios where the dumbbells are shorter, meaning the optimal 'X' configuration cannot be propagated throughout all particles. Even in the most elongated state the 'X' configuration is not observed past the 2-particle level, with each dumbbell pair interacting with neighbouring pairs in a frustrated near-parallel orientation. This then leaves the parallel, side-by-side configuration of dumbbells as the ideal configuration for packing efficiently. The planar structure had the lowest energy with a value of roughly -53ϵ , indicating that this structure is the most stable structure. The increasingly frustrated structures were increasingly less stable but within a close range of energies around -42ϵ .

It is clear from the global optimisation data that the geometric restrictions formed due to the elongation of the dumbbell particles drive the differences in energetically viable structure and therefore the local ordering of the systems. This is local ordering then dictates the differences seen in the microstructures of the quenched steady states, corroborating our hypothesis.

5.2.2. Quenched steady state under shear

An external shear was applied to the steady states of the temperature quenched systems. Figure 46a shows the RDF of the quenched $L^* = 0.2$ system under shear and we observe an increase in translational order as the shear rate is increased. Almost every peak increases in intensity with a notable decrease in the second peak of the RDF, corresponding to the loss of dumbbells in the 'T' configuration. This implies the system increases in orientational order in the presence of shear and suggests that the randomly ordered hexagonal closed-packed sheets have been able to rearrange from single sheets into more crystalline structures under shear. In the quenched steady state of the $L^* = 0.2$ system it appeared that the sheets were attached to one another only by a few dumbbell interactions. However, even these weak interactions could not be overcome at the low temperature that the system was quenched to. However, upon shearing the system, the external force allowed the system to escape this kinetic trap and achieve crystallisation.

Figure 46b shows the quenched $L^* = 0.8$ system under shear and we observe very little change in the translational order of the system at the first two applied shear rates. A small



Figure 46: Radial distribution functions for the systems of symmetric colloidal dumbbells under shear at varying shear rates from $\dot{\gamma} = 0.01$ to 10.0 for two different values of the aspect ratio L^* : (left) $L^* = 0.2$ and (right) $L^* = 0.8$.

decrease in order is observed at a shear rate of $\dot{\gamma} = 1.0$ and then a significant decrease in translational order is observed at the highest shear rate of $\dot{\gamma} = 10.0$. This suggests that the amorphous structure seen in the quenched state may be weakening under shear and reaching a breaking point at the highest shear rate in which the structure is becoming more fluid-like.



Figure 47: Orientational distribution functions for the systems of symmetric colloidal dumbbells under shear at varying shear rates from $\dot{\gamma} = 0.01$ to 10.0 for two different values of the aspect ratio L^* : (a) $L^* = 0.2$ and (b) $L^* = 0.8$.

Figure 47a shows the ODF analysis of the quenched $L^* = 0.2$ system under shear. There



Figure 48: Snapshots of representative configurations under shear at varying shear rates for the system of symmetric colloidal dumbbells with the aspect ratio $L^* = 0.2$ at the packing fraction $\phi_{\alpha} = 0.1$. The direction and velocity gradient of shear flow are labelled on each snapshot. NOTE: The dotted lines are purely a visual aid and is not a direct reflection of the simulation box.

is a clear increase in orientational order reflecting what was observed in the RDF data, including the small decrease in the negative peak at around r = 1.1 indicating the loss of particles in the 'T' configuration. This further corroborates the idea that the external shear flow is facilitating the crystallisation of the system. Figure 47b shows the ODF analysis of the quenched $L^* = 0.8$ system under shear showing very little change as the smaller rates of shear are applied to the system. When the highest shear rate of $\dot{\gamma} = 10$ was applied to the system, there was a decrease in orientational order. The ODF data matches well with the observations made in the analysis of the RDF data. Figure 48 shows snapshots of the $L^* = 0.2$ system under increasing shear rates. The snapshots show the hexagonal close-packed sheets of the quenched steady state being pushed into stacked planes and what appears to be crystalline structures. The visual inspection of the system greatly supports the observations made in the RDF and ODF analysis, where the external shear flow is facilitating the crystallisation of the kinetically trapped quenched system. A visual inspection of the snapshots clarify that, although the planar sheets are being pushed together, there does not appear to be a correlation between the direction of flow and the orientation of the stacked planes.

When the external shear is turned off from this crystalline system, the structure does not revert back to the quenched state before the shear was applied. The planar structure has undergone a plastic deformation and implies that the crystalline phase is the thermodynamically stable phase of the system. This corroborates well with the hypothesis that the quenched system was kinetically trapped from reaching the crystalline state and the external shear flow induces the process.

In order to confirm the onset of this shear-induced crystallisation in the low aspect ratio system, the average number of crystalline particles were identified in the structures obtained at each of the shear rates considered. This is done using well-established methods based on the Steinhardt bond-orientational order-parameters [127–129]. First, the complex vector \mathbf{q}_l is determined for each particle:

$$q_{lm}(i) = \frac{1}{N_{\rm B}} \sum_{j=1}^{N_{\rm B}(i)} Y_{lm}(\mathbf{r}_{ij})$$
(64)

where $N_{\rm B}$ is the number of first nearest-neighbors of particle *i* based on a radial cutoff $(r_{\rm c})$, \mathbf{r}_{ij} is the vector connecting the centres of particles *i* and *j* and Y_{lm} is the spherical

harmonic with symmetry index l and $-l \leq m \leq l$. Then, two particles are considered to share a crystalline bond if their local environments are sufficiently similar. This is determined using the translational-order correlation parameter:

$$d_l(i,j) = \operatorname{Re}\left(\frac{\mathbf{q}_l(i) \cdot \mathbf{q}_l^*(j)}{|\mathbf{q}_l(i)||\mathbf{q}_l(j)|}\right)$$
(65)

where the * indicates the complex conjugate and $\mathbf{q}_l(i) \cdot \mathbf{q}_l^*(j) = \sum_{m=-l}^{l} q_{lm}(i) \cdot q_{lm}^*(j)$. Following previous studies, the symmetry index is taken to be l = 6, and two particles are considered to share a crystalline bond if $d_6(i, j) \ge 0.7$. Finally, those particles which possess a certain threshold number of crystalline bonds, N_{cb} , are labelled as crystalline. As close-packed crystal motifs are expected to form the threshold number is chosen to be $N_{cb} = 8$ and the radial cutoff for determining nearest neighbours is set to be $r_c/\sigma = 1.2 + L^*$.



Figure 49: Evolution of (a) the average fraction of crystalline particles (f_{xtal}) and (b) the energy of the system along the simulation trajectory, as a function of shear rate for the system of symmetric colloidal dumbbells with an aspect ratio of $L^* = 0.2$ at a packing fraction of $\phi_{\alpha} = 0.1$.

Figure 49a shows the average fraction of crystalline particles (f_{xtal}) for structures obtained

at each of the shear rate considered for the system of dumbbells with an aspect ratio of $L^* = 0.2$. It is evident that there is a significant increase in f_{xtal} when $\dot{\gamma} = 10$, confirming the onset of shear-induced crystallisation.

Figure 49b shows the energy of the system of dumbbells with an aspect ratio of $L^* = 0.2$ along the simulation trajectories as the various shear rates were applied to the quenched steady state. Here we see a discontinuous phase transition upon application of the shear rate of $\dot{\gamma} = 10$, confirming that the system is clearly undergoing crystallisation. The lower shear rate of $\dot{\gamma} = 1$ also reaches the crystallised state but through multiple smaller energy drops along the trajectory. Although the lower two shear rates appear to drop the energy of the system, a clear phase transition is not apparent. The observation in energy closely ties in with the increase in the average fraction of crystalline particles in the system as a function of increasing shear rate, further proving the onset of shear-induced crystallisation.

The energy data presented in Figure 49b is not wholly convincing of the systems reaching a steady state by the end of the simulation trajectory. If a steady state is reached the energy of the system remains stable, and although the energies begin to settle by the end of the simulation trajectory, there are multiple small drops in energy that occur throughout the trajectories. Each system was simulated three times from three random starting configurations to observe whether the states reached in the presented work in Figure 49b are reproducible. Although none of the simulation trajectories showed especially stable energies, similar to that of the presented data, there was reasonable correlation in the final energies of the systems which lead to the conclusion that the simulations have most likely reached the steady state.



Figure 50: Snapshots of representative configurations under shear at varying shear rates for the system of symmetric colloidal dumbbells with the aspect ratio $L^* = 0.8$ at the packing fraction $\phi_{\alpha} = 0.1$. The direction and velocity gradient of shear flow are labelled on each snapshot. NOTE: The dotted lines are purely a visual aid and is not a direct reflection of the simulation box.

Figure 50 shows the snapshots of the $L^* = 0.8$ system under increasing shear rates. At the higher aspect ratio, the amorphous structure remains intact and is showing resistance to structural change at the smaller shear rates, reflecting the analysis of the RDF and ODF data. Further still at the highest shear rate, $\dot{\gamma} = 10$, we observe a collapse in the thick strand-like amorphous structure with the system instead forming an amorphous layer in the simulation box. The snapshots do not appear to reveal a direct dependence between the collapse of the microstructure with the direction of flow.

This collapse could suggest the presence of a yield stress which would be some evidence that the high aspect ratio regime undergoes gelation upon quenching, as a key property of a gel is to be resistant to shear strain up to a yield point that results in the collapse of the gel [126]. To confirm the presence of a yield stress, the external shear was turned off and the system allowed to return to a steady state. Once the system had reached a steady state without the external shear, it was observed that the system did not return to the original quenched state. The system has undergone a plastic deformation, confirming that the collapse of the thick strand-like amorphous structure is due to a yield stress, and adding to evidence for the formation of a colloidal gel structure.

Unfortunately, although there is some evidence, the finite-size effects of the small system size means that the data in this study alone cannot confirm the formation of a colloidal gel structure under the temperature quenching of attractive colloidal dumbbell particles at the high aspect ratio regime.

5.3. Conclusions

A Brownian Dynamics study was carried out on a system of symmetric dumbbells with varying elongation at a density of $\phi_{\alpha} = 0.1$. The systems were temperature quenched and resulted in two distinct kinetically arrested structures. As hypothesised, the utilisation of the shape anisotropy of the symmetric dumbbell particles introduced a bias in the local order in the system, leading to very interesting arrested microstructures as the systems were quenched.

At low aspect ratios planar structures were observed with high orientational order favouring the parallel configuration of neighbouring particles within each plane. A global optimisation study confirmed a hypothesis that the range of the depletion attraction between the symmetric dumbbell particles alongside the geometric restriction of the low aspect ratio drove the formation of planar structures of parallel dumbbells. It would be of interest, moving forward, to study the effect of adjusting the range of attraction on the planar structures as a function of aspect ratio. At higher aspect ratios strand-like amorphous structures were observed. It is difficult to fully ascertain if these structures are spacespanning as the presence of finite-size effects was not tested in the timeframe of this work. Larger system sizes must be studied in order to confirm the space-spanning behaviour of the system.

An external shear was applied to the temperature quenched systems. It was seen that the $L^* = 0.8$ was resistant to low shear rates and driven to plastic deformation at the highest applied rate of shear. With the potential space-spanning nature of the amorphous structure and the presence a yield stress, there is good evidence pointing to the formation of a colloidal gel structure following a temperature quench. However, the finite-size effect driven by the small system size makes it very difficult to correctly identify a space-spanning network as the periodic simulation box is simply too small. Further investigation of larger system sizes is required to be certain.

Most interestingly, at the low aspect ratio regime, the external shear facilitated the reorientation of the planar sheet structures into crystalline clusters. As the shear rate was increased there appeared to be a clear phase transition to a thermodynamically favourable crystalline structure. This suggests that the system exhibits shear-induced crystallisation when there is a small elongation to the dumbbells.

6. CONCLUSION

6.1. Summary

In this thesis, the rheological behaviour of suspensions of colloidal dumbbells interacting via depletion attractions was investigated, using Brownian Dynamics simulations. The colloidal dumbbells were treated as rigid bodies with two interaction sites located at the centres of the spherical lobes. The site-site interactions were described by the generalised Lennard-Jones potential with an exponent which is sufficiently high to describe the shortrange attractions. The focus was on understanding the effects of shape anisotropy on the rheological properties of the suspensions in connection with their microstructures so that the rheological behaviour can be controlled.

We considered dense suspensions of symmetric colloidal dumbbells and investigated the effects of shape anisotropy on the rheological behaviour of these suspensions. We observed a non-monotonic dependence of the equilibrium shear viscosity on the aspect ratio L^* as it was varied from 0.2 to 0.8. The non-monotonic dependence was most pronounced for the densest suspension considered, with the shear viscosity showing a minimum at an intermediate aspect ratio. We attributed this non-monotonic variation on competition between stronger correlations at low aspect ratio and slower decorrelations at high aspect ratio. Translation-rotation decoupling was also apparent in the system with a non-monotonic trend in the translation diffusion, mirroring that of the shear viscosity, and a monotonic trend in the rotational diffusion. Under an external shear flow, the suspensions exhibited shear thinning behaviour, which became more pronounced with increasing aspect ratio of the dumbbells. Our analysis reveals that the shear thinning behaviour was correlated with microstructures, where the axis of symmetry of the dumbbells tend to align with the direction of the shear flow and noticeable enhancement in layering along the shear gradient direction.

With the aim of controlling the microstructure, suspensions of asymmetric colloidal dumbbells were considered to promote self-limiting cluster formation upon gradual cooling. Here, we exploited the size ratio between the lobes and a hierarchy of strengths for the interactions between them to form self-limiting clusters in a controlled way. A gradual increase in the equilibrium shear viscosity was observed with the growth in the fraction of particles forming self-limiting clusters. Under an external shear flow, we observed a strong shear thinning behaviour, which was attributed to the disassembly of the clusters with increasing shear rate.

A dilute suspension of symmetric colloidal dumbbells was quenched from a high-temperature fluid phase in search of routes to gel in the presence of shape anisotropy. At low aspect ratios, hexagonal close-packed sheets of orientationally ordered dumbbells were formed after the temperature quench. With increasing aspect ratio, the local translational order became more frustrated forming an amorphous network. The change in local order was attributed to geometric restriction due to the elongation of the dumbbells making the energetically favourable sheet structure unavailable for the higher aspect ratio systems. When subjected to an external shear, we observed shear-induced crystallisation in the low aspect ratio regime, while distinct gel-like physical properties were on display at the higher aspect ratio regime. The change in local order due to shape anisotropy appeared to play a critical role in observing such differing and interesting microstructures following a temperature quench. This body of work has presented fundamental observations of novel systems, with several interesting observations made on the rheological properties alongside the reaction of the systems to an external shear. This computational work has laid the initial foundation of fundamental observations in hope that future work can provide key information for industrial processes and products.

6.2. Outlook

Several lines of inquiry worth further investigation have emerged from the present study.

- We observed a manifestation of translation-rotation decoupling in the system. It will be of utmost importance to ascertain the origin of this decoupling behaviour for fully understanding the effects of shape anisotropy on the rheological behaviour. Without fully understanding this behaviour it would not be possible to confidently transfer these observations to practical applications beyond the computational space.
- The design principles for self-limiting cluster formation demonstrated with asymmetric colloidal dumbbells need not be limited to tetrahedral cluster formation. It would be of interest to search the potential energy surface of the system to find parameters to achieve the self-limiting formation of different cluster sizes. This would allow for wider control of the microstructure of the colloidal suspensions, which would have great interest for practical applications such as drug delivery and oil recovery. It would also be important to conduct a further study of the tetrahedral cluster formation with stronger primary interactions, aiming to stabilise the clusters under shear in order to investigate the behaviour of the suspensions under

shear as a function of the fraction of particles forming the clusters. As shear forces are a constant presence in real systems, it would be important to maximise the stability of clusters under shear to increase the longevity of the clusters in practical applications.

- Upon quenching, the system of symmetric colloidal dumbbells was arrested into two very contrasting microstructures depending on the aspect ratio of the dumbbells. It would be important to establish if there are any finite-size effects on our results by investigating larger system sizes. With more information on finite-size effects we can solidify our claims of potential gel structures forming under quenching conditions. It would also be useful to ascertain the phase diagram of the quenched system and identify the cross-over region from crystalline stacked planes to an amorphous structure.
- A computational framework that can explicitly handle the hydrodynamic interactions between anisotropic colloidal particles in the suspensions will be vital to fully understand the rheological behaviour of suspensions of colloidal dumbbells and take this body of work to the next level. We have begun to develop a computational framework that implements the Dissipative Particle Dynamics (DPD) technique for suspensions of anisotropic colloidal particles, an explicit solvent technique, allowing for inclusion of the hydrodynamic interactions. Although primary work in this regard has proved promising, the current in-house framework requires further development to be able to treat the colloidal dumbbells in question. It will be important to carry on this development. Given in the appendix is a description of the theoretical framework for DPD along with initial developments and benchmarking.

LIST OF REFERENCES

- W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloid Dispersions*, (Cambridge University Press, 1991) p. 525.
- [2] P. Habdas and E. R. Weeks, "Video microscopy of colloidal suspensions and colloidal crystals," Current Opinion in Colloid Interface Science, 7, 196–203 (2002).
- [3] W. C. K. Poon, "Colloids as Big Atoms," Science, **304**, 830–831 (2004).
- [4] P. N. Pusey, W. C. K. Poon, S. M. Ilett, and P. Bartlett, "Phase behaviour and structure of colloidal suspensions," Journal of Physics: Condensed Matter, 6, A29–A36 (1994).
- [5] R. Mezzenga, P. Schurtenberger, A. Burbidge, and M. Michel, "Understanding foods as soft materials," Nature Materials, 4, 729–740 (2005).
- [6] O. Cohu and A. Magnin, "Rheometry of paints with regard to roll coating process," Journal of Rheology, 39, 767 (1995).
- [7] Y. Wang, I. C. Jenkins, J. T. McGinley, T. Sinno, and J. C. Crocker, "Colloidal crystals with diamond symmetry at optical lengthscales," Nature Communications, 8, 14173 (2017).
- [8] S. Mitragotri and J. Lahann, "Physical approaches to biomaterial design," Nature Materials, 8, 15–23 (2009).
- [9] G. Tang and N. R. Morrow, "Influence of Brine Composition and Fines Migration on Crude Oil/Brine/Rock Interactions and Oil Recovery," Journal of Petroleum Science and Engineering, 24, 99–111 (1999).
- [10] V. J. Anderson and H. N.W. Lekkerkerker, "Insights into phase transition kinetics from colloid science," Nature, 416, 811–815 (2002).
- [11] D. T. N. Chen, Q. Wen, P. A. Janmey, J. C. Crocker, and A. G. Yodh, "Rheology of Soft

Materials," Annual Review of Condensed Matter Physics, 1, 301–322 (2010).

- [12] B. Derjaguin and L. D. Landau, "Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes," Acta Physicochimica U.R.S.S., 14, 633–662 (1941).
- [13] E. J. W. Verwey and J. T. G. Overbeek, Theory of the stability of lyophobic colloids. The interaction of particles having an electric double layer, (Elsevier, 1948) p. 216.
- [14] S. Asakura and F. Oosawa, "On Interaction between Two Bodies Immersed in a Solution of Macromolecules," Journal of Chemical Physics, 22, 1255–1256 (1954).
- [15] A. Vrij, "Polymers at Interfaces and the Interactions in Colloidal Dispersions," Pure and Applied Chemistry, 48, 471–483 (1976).
- [16] K. Binder, P. Virnau, and A. Statt, "Perspective: The asakura oosawa model: A colloid prototype for bulk and interfacial phase behaviour," The Journal of Chemical Physics 141, 140901 (2014).
- [17] M. Dijkstra, J. M. Brader, and R. Evans, "Phase behaviour and structure of model colloid-polymer mixtures," Journal of Physics: Condensed Matter 11, 10079 (1999).
- [18] J. Taffs, A. Malins, S. R. Williams, and C. P. Royall, "A structural comparison of models of colloid-polymer mixtures," Journal of Physics: Condensed Matter, 22, 104119 (2010).
- [19] G. A. Vliegenthart, Lodge J. F. M., and H. N. W. Lekkerkerker, "Strong weak and metastable liquids structural and dynamical aspects of the liquid state," Physica A 263, 378–388 (1999).
- [20] W. C. K. Poon, "The physics of a model colloid polymer mixture," Journal of Physics: Condensed Matter, 14, R859–R880 (2002).
- [21] C. E. Chaffey, "Mechanisms and equations for shear thinning and thickening in disper-

sions," Colloid and Polymer Science, 255, 691–698 (1977).

- [22] N. J. Wagner and J. F. Brady, "Shear thickening in colloidal dispersions," Physics Today, 62, 27–32 (2009).
- [23] X. Xu, S. A. Rice, and A. R. Dinner, "Relation between ordering and shear thinning in colloidal suspensions," Proceedings of the National Academy of Sciences of the United States of America, 110, 3771–3776 (2013).
- [24] W. Pan, B. Caswell, and G. E. Karniadakis, "Rheology, Microstructure and Migration in Brownian Colloidal Suspensions," Langmuir, 26, 133–142 (2010).
- [25] X. Cheng, J. H. McCoy, J. N. Israelachvili, and I. Cohen, "Imaging the microscopic structure of shear thinning and thickening colloidal suspensions," Science, 333, 1276–1279 (2011).
- [26] P. N. Pusey and W. van Megen, "Phase behaviour of concentrated suspensions of nearly hard colloidal spheres," Nature, **320**, 340–342 (1986).
- [27] G. Petekidis, D. Vlassopoulos, and P. N. Pusey, "Yielding and flow of sheared colloidal glasses," Journal of Physics: Condensed Matter, 16, S3955–S3963 (2004).
- [28] B. M. Guy, M. Hermes, and W. C. K. Poon, "Towards a Unified Description of the Rheology of Hard-Particle Suspensions," Physical Review Letters, 115, 088304 (2015).
- [29] A. Einstein, "Berichtigung zu meiner Arbeit: "Eine neue Bestimmung der Moleküldimensionen"," Annalen der Physik, 339, 591 (1911).
- [30] G. K. Batchelor and J. T. Green, "The determination of the bulk stress in a suspension of spherical particles to order," Journal of fluid mechanics 56, 401–427 (1972).
- [31] C. I. Mendoza and I. Santamaria-Holek, "The rheology of hard sphere suspensions at arbitrary volume fractions: An improved differential viscosity model," The Journal of

Chemical Physics **130**, 044904 (2009).

- [32] I. M. Krieger, "Rheology of monodisperse latices," Advances in Colloid and Interface Science, 3, 111–136 (1972).
- [33] H. N. W. Lekkerkerker, W. C. K. Poon, P. N. Pusey, A. Stroobants, and P. B. Warren,
 "Phase Behaviour of Colloid + Polymer Mixtures," Europhysics Letters, 20, 559–564 (1992).
- [34] B. Vincent, J. Edwards, S. Emmett, and R. Croot, "Phase separation in dispersions of weakly-interacting particles in solutions of non-adsorbing polymer," Colloids and Surfaces, 31, 267–298 (1988).
- [35] F. L. Calderon, J. Bibette, and J Biais, "Experimental Phase Diagrams of Polymer and Colloid Mixtures," Europhysics Letters, 23, 653–659 (1993).
- [36] J. Sabin, A. E. Bailey, and B. J. Frisken, "Exploring the dynamics of phase separation in colloid–polymer mixtures with long range attraction," Soft Matter, 12, 5325–5333 (2016).
- [37] L. Feng, B. Laderman, S. Sacanna, and P. Chaikin, "Re-entrant solidification in polymer-colloid mixtures as a consequence of competing entropic and enthalpic attractions," Nature Materials, 14, 61–65 (2014).
- [38] L. Rossi, S. Sacanna, W. T. M. Irvine, P. M. Chaikin, D. J. Pine, and A. P. Philipse, "Cubic crystals from cubic colloids," Soft Matter, 7, 4139–4142 (2011).
- [39] S. Sacanna, W. T. M. Irvine, P. M. Chaikin, and D. J. Pine, "Lock and key colloids," Nature, 464, 575–578 (2010).
- [40] R. W. Perry, G. Meng, T. G. Dimiduk, J. Fung, and V. N. Manoharan, "Real-space studies of the structure and dynamics of self-assembled colloidal clusters," Faraday Discussions, 159, 211–234 (2012).
- [41] W. C. K. Poon, "Colloidal Glasses," MRS Bulletin, **29**, 96–99 (2004).
- [42] E. Zaccarelli, "Colloidal gels: equilibrium and non-equilibrium routes," Journal of Physics: Condensed Matter, 19, 323101 (2007).
- [43] D. Marzi, B. Capone, J. Marakis, M. C. Merola, D. Truzzolillo, L. Cipelletti, F. Moingeon, M. Gauthier, D. Vlassopoulos, C. N. Likos, and M. Camargo, "Depletion, melting and reentrant solidification in mixtures of soft and hard colloids." Soft matter, **11**, 8296–8312 (2015).
- [44] R. Harich, A. Deblais, A. Colin, and H. Kellay, "Depletion forces induce visco-elastocapillary thinning of non-Brownian suspensions," Europhysics Letters, 114, 58006 (2016).
- [45] R. Harich, T. W. Blythe, M. Hermes, E. Zaccarelli, A. J. Sederman, L. F. Gladden, and W. C. K. Poon, "Gravitational collapse of depletion-induced colloidal gels," Soft Matter, 12, 4300–4308 (2016).
- [46] M. Laurati, G. Petekidis, N. Koumakis, F. Cardinaux, A. B. Schofield, J. M. Brader,
 M. Fuchs, and S. U. Egelhaaf, "Structure, dynamics, and rheology of colloid-polymer
 mixtures: From liquids to gels," Journal of Chemical Physics, 130, 134907 (2009).
- [47] L. Onsager, "The effects of shape on the interaction of colloidal particles," Annals of the New York Academy of Sciences, 51, 627–659 (1949).
- [48] H. Lowen, "Brownian dynamics of hard spherocylinders," Physical Review E, 50, 1232– 1242 (1994).
- [49] J. Schwarz-Linek, C. Valeriani, A. Cacciuto, M. E. Cates, D. Marenduzzo, A. N. Morozov, and W. C. K. Poon, "Phase separation and rotor self-assembly in active particle suspensions," Proceedings of the National Academy of Sciences of the United States of America, 109, 4052–4057 (2012).

- [50] P. Bolhuis and D. Frenkel, "Tracing the phase boundaries of hard spherocylinders," Journal of Chemical Physics, 106, 666–687 (1997).
- [51] D. Frenkel, B. M. Mulder, and McTague J. P., "Phase diagram of a system of hard ellipsoids," Physical Review Letters, 52, 287–290 (1984).
- [52] A. Kuijk, D. V. Byelov, A. V. Petukhov, A. van Blaaderen, and A. Imhof, "Phase behaviour of colloidal silica rods," Faraday Discussions, 159, 181–199 (2012).
- [53] L. G. Leal and E. J. Hinch, "The rheology of a suspension of nearly spherical particles subject to Brownian rotations," Journal of Fluid Mechanics, 55, 745 (1972).
- [54] A. Overbeck, "Ueber stationäre flüssigkeitsbewegungen mit berücksichtigung der inneren reibung," Journal für die reine und angewandte Mathematik, 81, 62 (1876).
- [55] G. B. Jeffery, "The motion of ellipsoidal particles immersed in a viscous fluid," Proceedings of the Royal Society A, 102, 161 (1922).
- [56] G. I. Taylor, "The motion of ellipsoidal particles in a viscous fluid," Proceedings of the Royal Society A, 103, 58 (1923).
- [57] E. Y. Harper and I. D. Chang, "Maximum dissipation resulting from lift in a slow viscous shear flow," Journal of fluid mechanics, 33, 209 (1968).
- [58] P. Brunn, "The slow motion of a rigid particle in a second-order fluid," Journal of fluid mechanics, 82, 529 (1977).
- [59] D. Z. Gunes, R. Scirocco, J. Mewis, and Vermant. J., "Flow-induced orientation of nonspherical particles: Effect of aspect ratio and medium rheology," Journal of non-newtonian fluid mechanics, 155, 39 (2008).
- [60] G. D'avino, M. A. Hulsen, F. Greco, and P. L. Maffettone, "Bistability and metabistability scenario in the dynamics of an ellipsoidal particle in a sheared viscoelastic fluid," Physical

Review E, **89**, 043006 (2014).

- [61] H. Brenner, "Rheology of a dilute suspension of axisymmetric Brownian particles," Journal of Multiphase Flow, 1, 195 (1973).
- [62] P. M. Johnson, C. M. van Kats, and A. van Blaaderen, "Synthesis of colloidal silica dumbbells," Langmuir, 21, 11510–11517 (2005).
- [63] D. Nagao, C. M. van Kats, K. Hayasaka, M. Sugimoto, M. Konno, A. Imhof, and A. van Blaaderen, "Synthesis of hollow asymmetrical silica dumbbells with a movable inner core," Langmuir, 26, 5208–5212 (2010).
- [64] F. Chu, M. Siebenburger, F. Polzer, C. Stolze, J. Kaiser, M. Hoffmann, N. Heptner, J. Dzubiella, M. Drechsler, Y. Lu, and M. Balluff, "Synthesis and characterization of monodisperse thermosensitive dumbbell-shaped microgels," Macromolecular Rapid Communications, **33**, 1042–1048 (2012).
- [65] B. Peng, H. R. Vutukuri, A. van Blaaderen, and A. Imhof, "Synthesis of fluorescent monodisperse non-spherical dumbbel-like model colloids," Journal of Materials Chemistry, 22, 21893–21900 (2012).
- [66] C. Vega, E. P. A. Paras, and P. A. Monson, "Solid-fluid equilibria for hard dumbbells via Monte Carlo simulation," Journal of Chemical Physics, 96, 9060 (1992).
- [67] C. Vega and P. A. Monson, "Plastic crystal phases of hard dumbbells and hard spherocylinders," Journal of Chemical Physics, 107, 2696 (1997).
- [68] M. Marechal and M. Dijkstra, "Stability of orientationally disordered crystal structures of colloidal hard dumbbells"," Physical Review E, 77, 061405 (2008).
- [69] N. Heptner and J. Dzubiella, "Equilibrium structure and fluctuations of suspen- sions of colloidal dumbbells," Molecular Physics, 113, 2523–2530 (2015).

- [70] N. Heptner, F. Chu, Y. Lu, P. Lindner, M. Ballauff, and J. Dzubiella, "Nonequilibrium structure of colloidal dumbbells under oscillatory shear," Physical Review E, 92, 052311 (2015).
- [71] B. Z. Dlugogorski, M. Grmela, and P. J. Carreau, "Viscometric functions for FENE and generalized Lennard-Jones dumbbell liquids in Couette flow: molecular dynamics study," Journal of Non-Newtonian Fluid Mechanics, 48, 303 (1993).
- [72] E. Sultan, J. W. van de Meent, E. Somfai, A. N. Morozov, and W. van Saarloos, "Polymer rheology simulations at the meso- and macroscopic scale," Europhysics Letters, 90, 64002 (2010).
- [73] A. K. Townsend and H. J. Wilson, "Small- and large-amplitude oscillatory rheometry with bead–spring dumbbells in Stokesian Dynamics to mimic viscoelasticity," Journal of Non-Newtonian Fluid Mechanics, 261, 136 (2018).
- [74] S. Mandal and D. V. Khakhar, "A study of the rheology of planar granular flow of dumbbells using discrete element method simulations," Physics of Fluids, 28, 136 (2016).
- [75] S. Mandal and D. V. Khakhar, "A study of the rheology and micro-structure of dumbbells in shear geometries," Physics of Fluids, **30**, 013303 (2018).
- [76] C. N. Likos, "Effective interactions in soft condensed matter physics," Physics Reports, 348, 267–439 (2001).
- [77] J. A. Barker and D. Henderson, "Pertubation theory and equation of state for fluids. ii. a successful theory of liquids," Journal of Chemical Physics, 47, 4714–4721 (1967).
- [78] D. Chakrabarti, GlOSP: A program for Global Optimisation for Structure Prediction.
- [79] S. N. Fejer, D. Chakrabarti, and D. J. Wales, "Self-assembly of anisotropic particles," Soft Matter, 7, 3553–3564 (2011).

- [80] D. J. Wales and H. A. Scheraga, "Global optimisation of clusters, crystals, and biomolecules," Science, 285, 1368–1372 (1999).
- [81] D. C. Liu and J. Nocedal, "On the limited memory bfgs method for large scale optimisation," Mathematical Programming, 45, 503–528 (1989).
- [82] D. J. Wales and J. P. K. Doye, "Global optimisation by basin-hopping and the lowest energy structures of lennard-jones clusters containing up to 110 atoms," Journal of Physical Chemistry A, 101, 5111–5116 (1997).
- [83] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, "Equation of state calculations by fast computing machines," Journal of Chemical Physics, 21, 1087–1092 (1953).
- [84] M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids, 2nd ed. (Oxford University Press, 2017).
- [85] J. M. Van der Veer, "On brownian dynamics simulations of concentrated dispersions," (1992).
- [86] A. W. Lees and S. F. Edwards, "The computer study of transport processes under extreme conditions," Journal of Physics C: Solid State Physics, 5, 1921–1928 (1972).
- [87] P. J. Mitchell, D. M. Heyes, and J. R. Melrose, "Brownian-dynamics simulations of model stabilised colloidal dispersions under shear," Journal of the Chemical Society, Faraday Transactions, **91**, 1975–1989 (1995).
- [88] S. R. Rastogi, N. J. Wagner, and S. R. Lustig, "Rheology, self-diffusion, and microstructure of charged colloids under simple shear by massively parallel nonequilibrium brownian dynamics," The Journal of Chemical Physics, 104, 9234–9248 (1996).
- [89] D. Chandler, Introduction to modern statistical mechanics (Oxford University Press, 1987).

- [90] J. H. Irving and J. G. Kirkwood, "The statistical mechanical theory of transport processes.iv. the equations of hydrodynamics," Journal of Chemical Physics, 18, 817–829 (1950).
- [91] J. Rotne and S. Prager, "Variational treatment of hydrodynamic interactions in polymers," The Journal of Chemical Physics, 50, 4831–4837 (1969).
- [92] H. Yamakawa, "Transport properties of polymer chains in dilute solution: Hydrodynamic interaction," The Journal of Chemical Physics, 53, 436–443 (1970).
- [93] P. J. Zuk, E. Wajnryb, K. A. Mizerski, and P. Szymczak, "Rheology, self-diffusion, and microstructure of charged colloids under simple shear by massively parallel nonequilibrium brownian dynamics," Journal of Fluid Mechanics, 741, R5 (2014).
- [94] J. Garcia de la Torre and B. Carrasco, "Improved hydrodynamic interaction in macromolecular bead models," The Journal of Chemical Physics, 111, 4817–4826 (1999).
- [95] J-. W. Kim, R. J. Larsen, and D. A. Weitz, "Synthesis of nonspherical colloidal particles with anisotropic properties," Journal of the American Chemical Society, **128**, 14374–14377 (2006).
- [96] C. Vega, E. P. A. Paras, and P. A. Monson, "On the stability of the plastic crystal phase of hard dumbbell solids," The Journal of Chemical Physics, 97, 8543–8548 (1992).
- [97] K. Zhang, "On the concept of static structure factor," arXiv:1606.03610 (2016).
- [98] S. H. Chong and W. Gotze, "Idealised glass transitions for a system of dumbbell molecules," Physical Reveiw E, 65, 041504 (2002).
- [99] H-. X. Zhou, "Calculation of translational friction and intrinsic viscosity. 1. general formulation for arbitrarily shaped particles," Biophysical Journal, 69, 2286–2297 (1995).
- [100] D. M. Heyes and P. J. Mitchell, "Linear viscoelasticity of concentrated hard-sphere dispersions," Journal of Physics: Condensed Matter, 6, 6423–6436 (1994).

- [101] P. H. Mortensen, H. I. Andersson, J. J. J. Gillissen, and B. J. Boersma, "On the orientation of ellipsoidal particles in a turbulent shear flow," International Journal of Multiphase Flow, 34, 678–683 (2008).
- [102] J. Einarsson, J. R. Angilella, and B. Mehlig, "Orientational dynamics of weakly inertial axisymmetric particles in steady viscous flows," Physica D: Nonlinear Phenomena, 279, 79–85 (2014).
- [103] G. A. Voth, "Disks aligned in a turbulent channel," Journal of Fluid Mechanics, 772, 1–4 (2015).
- [104] A. Eshghinejadfard, S. A. Hosseini, and D. Thévenin, "Fully-resolved prolate spheroids in turbulent channel flows: A lattice boltzmann study," AIP Advances, 7, 095007 (2017).
- [105] E. Dickinson, Colloids in Food, (Applied Science, 1982) p. 533.
- [106] M. Dennison, K. Milinkovic, and M. Dijkstra, "Phase diagram of hard snowman-shaped particles," Journal of Chemical Physics, 137, 044507 (2012).
- [107] K. Milinkovic, M. Dennison, and M. Dijkstra, "Phase diagram of hard asymmetric dumbbell particles," Physical Review E, 87, 032128 (2013).
- [108] D. Morphew and D. Chakrabarti, "Hierarchical self-assembly of colloidal magnetic particles into reconfigurable spherical structures." Nanoscale, 7, 8343–50 (2015).
- [109] S. Peng, F. Smallenburg, A. Imhof, M. Dijkstra, and A. van Blaaderen, "Colloidal clusters by using emulsions and dumbbell-shaped particles: experiments and simulations," Angewandte Chemie International Edition, 52, 6709–6712 (2013).
- [110] G. Avvisati, T. Vissers, and M. Dijkstra, "Self-assembly of patchy colloidal dumbbells," Journal of Chemical Physics, 142, 084905 (2015).
- [111] D. Morphew, J. Shaw, C. Avins, and D. Chakrabarti, "Programming hierarchical self-

assembly of patchy particles into colloidal crystals via colloidal molecules," ACS Nano, 12, 2355–2364 (2018).

- [112] A. B. Rao, J. Shaw, A. Neophytou, D. Morphew, F. Sciortino, R. L. Johnston, and D. Chakrabarti, "Leveraging hierarchical self-assembly pathways for realizing colloidal photonic crystals," ACS Nano, 14, 5348–5359 (2020).
- [113] Q. Chen, E. Diesel, J. K. Whitmer, S. C. Bae, E. Luijten, and S. Granick, "Triblock colloids for directed self-assembly," Journal of the American Chemical Society, 133, 7725– 7727 (2011).
- [114] P. L. Chau and A. J. Hardwick, "A new order parameter for tetrahedral configurations," Molecular Physics, 93, 511–518 (1998).
- [115] J. R. Errington and P. G. Debenedetti, "Relationship between structural order and the anomalies of liquid water," Nature, 409, 318–321 (2001).
- [116] S. L. Lee, P. G. Debenedetti, and J. R. Errington, "A computational study of hydration, solution structure, and dynamics in dilute carbohydrate solutions," Journal of Chemical Physics, **122**, 204511 (2005).
- [117] D. R. Nutt and J. C. Smith, "Dual function of the hydration layer around an antifreeze protein revealed by atomistic molecular dynamics simulations," Journal of the American Chemical Society, 130, 13066–13073 (2008).
- [118] P. J. Lu, E. Zaccarelli, F. Ciulla, A. B. Schofield, F. Sciortino, and D. A. Weitz, "Gelation of particles with short-range attraction," Nature, 453, 499–503 (2008).
- [119] G. M. H. Wilkins, P. T. Spicer, and M. J. Solomon, "Colloidal system to explore structural and dynamical transitions in rod networks, gels, and glasses," Langmuir, 25, 8951–8959 (2009).

- [120] M. J. Solomon and P. T. Spicer, "Microstructural regimes of colloidal rod suspensions, gels, and glasses," Soft Matter, 6, 1391–1400 (2010).
- [121] R. P. Murphy, K. Hong, and N. J. Wagner, "Thermoreversible gels composed of colloidal silica rods with short-range attractions," Langmuir, **32**, 8424–8435 (2016).
- [122] C. Ferreiro-Cordova, C. P. Royall, and J. S. van Duijneveldt, "Anisotropic viscoelastic phase separation in polydisperse hard rods leads to nonsticky gelation," Proceedings of the National Academy of Sciences of the United States of America, **117**, 3415–3420 (2020).
- [123] C. P. Royall and A. Malins, "The role of quench rate in colloidal gels," Faraday Discussions, 158, 301–311 (2012).
- [124] Y. M. Joshi, "Dynamics of colloidal glasses and gels," The Annual Review of Chemical and Biomolecular Engineering, 5, 181–202 (2014).
- [125] H. Shintani and H. Tanaka, "Frustration on the way to crystallization in glass," Nature Physics, 2, 200–206 (2006).
- [126] J. F. M. Lodge and D. M. Heyes, "Transient colloidal gels by brownian dynamics computer simulation," Phyical Chemistry Chemical Physics, 1, 2119–2130 (1999).
- [127] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, "Bond-orientational order in liquids and glasses," Physical Review B 28, 784–805 (1983).
- [128] S. Auer and D. Frenkel, "Numerical prediction of absolute crystallization rates in hardsphere colloids," Journal of Chemical Physics 120, 3015–3029 (2004).
- [129] W. Lechner and C. Dellago, "Accurate determination of crystal structures based on averaged local bond order parameters," Journal of Chemical Physics 129, 114707 (2008).
- [130] D. S. Bolintineanu, G. S. Grest, J. B. Lechman, F. Pierce, S. J. Plimpton, and P. R. Schunk, "Particle dynamics modeling methods for colloid suspensions," Computational

Particle Mechanics, 1, 321–356 (2014).

- [131] P. J. Hoogerbrugge and J. M. V. A. Koelman, "Simulating Microscopic Hydrodynamic Phenomena with Dissipative Particle Dynamics," Europhysics Letters, 19, 155–160 (1992).
- [132] B. J. Alder and T. E. Wainwright, "Studies in molecular dynamics. General method," Journal of Chemical Physics, **31**, 459–466 (1959).
- [133] P. Español and P. Warren, "Statistical Mechanics of Dissipative Particle Dynamics," Europhysics Letters, 30, 191–196 (1995).
- [134] E. S. Boek, P. V. Coveney, H. N. W. Lekkerkerker, and P. Van der Schoot, "Simulating the rheology of dense colloidal suspensions using dissipative particle dynamics," Physical Review E, 55, 3124–3133 (1997).
- [135] N. Phan-Thien, N. Mai-Duy, and B. C. Khoo, "A spring model for suspended particles in dissipative particle dynamics," Journal of Rheology, 58, 839–867 (2014).
- [136] P. J. Hoogerbrugge and J. M. V. A. Koelman, "Dynamic Simulations of Hard-Sphere Suspensions Under Steady Shear," Europhysics Letters, 21, 363–368 (1993).
- [137] P. Español, "Fluid particle model," Physical Review E, 57, 2930–2948 (1997).
- [138] V. Pryamitsyn and V. Ganesan, "A coarse-grained explicit solvent simulation of rheology of colloidal suspensions," Journal of Chemical Physics, **122**, 104906 (2005).
- [139] W. Pan, I. V. Pivkin, and G. E. Karniadakis, "Single-particle hydrodynamics in DPD: A new formulation," Europhysics Letters, 84, 10012 (2008).
- [140] R. Kubo, "The fluctuation-dissipation theorem," Reports on Progress in Physics, 29, 255–283 (1966).
- [141] C. P. Lowe, "An alternative approach to dissipative particle dynamics," Europhysics Letters, 47, 145 (1999).

- [142] S. D. Stoyanov and R. D. Groot, "From molecular dynamics to hydrodynamics: A novel Galilean invariant thermostat," Journal of Chemical Physics, 122, 114112 (2005).
- [143] E. Peters, "Elimination of time step effects in DPD," Europhysics Letters, 66, 311–317 (2004).
- [144] L. Verlet, "Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules," Physical Review, 159, 98–103 (1967).
- [145] G. Besold, I. Vattulainen, M. Karttunen, and J. M. Polson, "Towards better integrators for dissipative particle dynamics simulations," Physical Review E, 62, R7611–R7614 (2000).
- [146] J. B. Gibson, K. Chen, and S. Chynoweth, "The equilibrium of a velocity-verlet type algorithm for DPD with finite time steps," International Journal of Modern Physics C, 10, 241–261 (1999).
- [147] R. D. Groot and P. B. Warren, "Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation," Journal of Chemical Physics, 107, 4423 (1997).
- [148] B. Leimkuhler and X. Shang, "On the numerical treatment of dissipative particle dynamics and related systems," Journal of Computational Physics, 280, 72–95 (2015).
- [149] B. Leimkuhler and X. Shang, "Pairwise adaptive thermostats for improved accuracy and stability in dissipative particle dynamics," Journal of Computational Physics, **324**, 174– 193 (2016).
- [150] A. Chaudhri and J. R. Lukes, "Velocity and Stress Autocorrelation Decay in Isothermal Dissipative Particle Dynamics," Physical Review E, 81, 026707 (2010).
- [151] M. S. Green, "Markoff Random Processes and the Statistical Mechanics of Time-Dependent Phenomena. II. Irreversible Processes in Fluids," Journal of Chemical Physics, 22, 398–413 (1954).

- [152] R. Kubo, "Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems," Journal of the Physical Society of Japan, 12, 570–586 (1957).
- [153] R. Kubo, M. Yokota, and S. Nakajima, "Statistical-Mechanical Theory of Irreversible Processes. II. Response to Thermal Disturbance," Journal of the Physical Society of Japan, 12, 1203–1211 (1957).
- [154] M. A. Seaton, R. L. Anderson, S. Metz, and W. Smith, "DL_MESO: highly scalable mesoscale simulations," Molecular Simulation, **39**, 796–821 (2013).
- [155] J. A. Backer, C. P. Lowe, H. C. J. Hoefsloot, and P. D. Iedema, "Poiseuille flow to measure the viscosity of particle model fluids," Journal of Chemical Physics, 122, 154503 (2005).
- [156] A. Chatterjee, "Modification to Lees–Edwards periodic boundary condition for dissipative particle dynamics simulation with high dissipation rates," Molecular Simulation, 33, 1233– 1236 (2007).

APPENDIX

Developing an in-house dissipative particle dynamics framework for the study of rheological properties of colloidal suspensions

Many successful computational studies of the rheology of colloidal suspensions have been done using implicit solvent techniques. However, the fit to experimental data has not been perfect and some observations have been contradictory [22, 23, 130]. The Brownian Dynamics framework used throughout this thesis is also an implicit solvent technique and there have been clear limitations and unanswerable questions that stem from the lack of hydrodynamic behaviour in the simulation. Even though the solvent is taken into account to some level, it is impossible to simulate the full picture of how the solvent is effecting the dynamics of the system without including the hydrodynamics. An obvious improvement would be to use an explicit solvent technique to refine the simulation data to better fit the experimental work.

To conserve the hydrodynamic behaviour of a system, it is essential to model the solvent explicitly. Looking at the solvent explicitly requires the simulation of the system to contain a large number of particles. Molecular Dynamics is one such technique, however, that framework has a large computational inefficiency in simulating the solvent around the colloidal particles. In 1992, Hoogerbrugge and Koelman [131] developed Dissipative Particle Dynamics (DPD) as an effective technique to study the hydrodynamics of complex fluids at the mesoscopic scale. It has strong ties to Molecular Dynamics (MD), a well documented method to study the time-dependent behaviour of molecular systems, first applied in the 1950's by Alder and Wainwright [132]. Dissipative Particle Dynamics is a technique that partitions the solvent into groups of solvent particles that are coarsegrained into discrete particles, coined "DPD particles".

The DPD particles have short-range interactions under a soft potential, given in equation (66). The soft potential means that the coarse-grained solvent particles are able to pass through each other, allowing for faster equilibration and larger time-steps to be used in the simulation. This is a major improvement to that of MD, where cumulative errors mean that a large time-step cannot be used in simulation. As colloidal systems are generally in the mesoscopic scale, it is absolutely important that the modelling technique can handle larger time-steps to capture the colloidal dynamics.

$$U_{r_{ij}} = \begin{cases} \frac{1}{2}a_{ij}r_c(1 - \frac{r_{ij}}{r_c})^2, & \text{if } r_{ij} < r_c \\ 0, & \text{if } r_{ij} \ge r_c \end{cases}$$
(66)

where a_{ij} is the strength of the repulsion between the *i*-th and *j*-th particle, r_c is a cutoff distance for the potential, and r_{ij} is the distance between the two particles.

This method vastly reduces the number of particles in the system needed for the simulation, alleviating the computational cost but maintaining the hydrodynamic information of the system. In the original form of DPD [131], there was no clear definition of the temperature of the system, and so the relationship between the temperature and the model parameters was not defined. Without this temperature relation, it is not possible to look at the thermodynamics of the model which is absolutely necessary for simulating colloidal systems. An advance in the model was made by Español and Warren [133] in 1995 where they derive the Fokker-Planck equation to give a defined temperature to the method. The original DPD method is a solvent-only technique and developments have been made to include colloidal particles in a suspension of DPD particles. It is common to simulate the colloid as a frozen collection of solvent particles and has been studied fairly extensively [130, 134–136]. The colloid can be simulated as one single hard-sphere, greatly reducing the computational cost of the simulations. One such method is the Fluid Particle Model and modifications [137–139].

The aim of this chapter is to develop an in-house framework for the DPD method. The previous studies in this thesis have all demonstrated the necessity for a simulation technique that can take hydrodynamic behaviour into account in order to fully understand the complex and interesting observations. The reason to develop an in-house framework is in order to have control over the way in which the model can be manipulated to use for simulations of novel systems, which can often be difficult in external programs.

Methodology

Standard DPD

Following the work of Español and Warren [133], we get the definition of the total force acting on a given coarse-grained DPD particle "i" in equation (67).

$$\boldsymbol{F}_{i} = \sum_{j \neq i} (\boldsymbol{F}_{ij}^{C} + \boldsymbol{F}_{ij}^{D} + \widetilde{\boldsymbol{F}}_{ij})$$
(67)

where F_{ij}^C gives the conservative force derived from the potential, given in equation (66), felt by the *i*-th particle due to the *j*-th particle in the system, F_{ij}^D denotes the dissipative force and \tilde{F}_{ij} describes the corresponding random force. These forces are shown in the following equations:

$$\boldsymbol{F}_{ij}^{C} = \begin{cases} a_{ij} (1 - \frac{r_{ij}}{r_c}) \hat{\boldsymbol{r}}_{ij}, & \text{if } r_{ij} < r_c \\ 0, & \text{if } r_{ij} \ge r_c \end{cases}$$
(68)

$$\boldsymbol{F}_{ij}^{D} = -\gamma \left[f(r) \right]^{2} (\hat{\boldsymbol{r}}_{ij} \cdot \boldsymbol{v}_{ij}) \hat{\boldsymbol{r}}_{ij}$$
(69)

$$\widetilde{\boldsymbol{F}}_{ij} = \widetilde{\sigma} \big[f(r) \big] \hat{\boldsymbol{r}}_{ij} \delta r \tag{70}$$

where the relative positions and velocities are given by vectors $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ (following Galilean invariance), the unit vector from \mathbf{r}_i to \mathbf{r}_j is given by $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$. Parameters γ and $\tilde{\sigma}$ represent the strengths of the dissipative and random forces respectively. δr is a Gaussian random number is zero mean and unit variance. [f(r)] is a position-dependent weight function which ensure that the dissipative and random forces are zero when $r_{ij} \geq r_c$.

Español and Warren [133] used the fluctuation-dissipation theorem to derive the relationship of the system parameters with temperature, given in equation (71) [140].

$$\widetilde{\sigma}^2 = 2\gamma k_B T \tag{71}$$

Following from this, the weight function is simply defined as seen in equation (72).

$$\left[f(r)\right] = 1 - \frac{r_{ij}}{r_c} \tag{72}$$

As well as following the fluctuation-dissipation theorem, the weight function gives the DPD particles an effective radius of 1 with the units of the cutoff radius, r_c .

Instead of using the overdamped limit, utilised by Brownian Dynamics, DPD uses Newton's equations of motion to propagate the model system [131, 133]. The technique used for the propagation of the system is called an integrator. There are some novel integrators for the DPD system [141–143], but the most common integrator using the equations of motion is called the Velocity Verlet integrator, developed by Verlet [144] and improved upon by Besold *et al.* [145].

Velocity Verlet integrator

There are many variations to the Velocity Verlet integrator available to be paired with DPD [145–147]. Below is a simple explanation of the basic form of the Velocity Verlet integrator.

The equations of motion are derived from Newton's Second law of motion as shown below.

$$\boldsymbol{F}_i = m_i \boldsymbol{a}_i \tag{73}$$

$$\boldsymbol{a}_i = \frac{\delta \boldsymbol{v}_i}{\delta t} \tag{74}$$

$$\boldsymbol{v}_i = \frac{\delta \boldsymbol{r}_i}{\delta t} \tag{75}$$

$$\delta \boldsymbol{v}_i = \frac{\boldsymbol{F}_i(t)}{m_i} \delta t \tag{76}$$

$$\delta \boldsymbol{r}_i = \boldsymbol{v}_i \delta t \tag{77}$$

Following equations (76) and (77), we can calculate how the positions and velocity would change over time. This brings us to the main part of the integrator seen in equations (78)-(80).

$$\boldsymbol{v}_i(t+\frac{1}{2}\Delta t) = \boldsymbol{v}_i(t) + \frac{1}{2}\Delta t \frac{\boldsymbol{F}_i(t)}{m_i}$$
(78)

$$\boldsymbol{r}_i(t + \Delta t) = \boldsymbol{r}_i(t) + \Delta t \boldsymbol{v}_i(t + \frac{1}{2}\Delta t)$$
(79)

$$\boldsymbol{v}_i(t+\Delta t) = \boldsymbol{v}_i(t+\frac{1}{2}\Delta t) + \frac{1}{2}\Delta t \frac{\boldsymbol{F}_i(t+\Delta t)}{m_i}$$
(80)

 Δt is the time-step parameter of the simulation. Once the system parameters have been defined, initial positions and velocities would need to be created and assigned to each particle in the system for the start of the simulation. After the initialisation, the total force can be calculated, followed by the mid-step velocity (equation (78)). Using this new velocity, the new positions for the particles can be calculated (equation (79)). The particles can then be moved to their new positions with boundary conditions taken into consideration if needed for the simulation. The total force is recalculated with the new positions and mid-step velocities. Finally, the velocity at the full time-step can be calculated (equation (80)). The process is cycled from the calculation of the mid-step velocity until the number of time-steps defined for the simulation is reached.

The Velocity Verlet integrator is a simple integrator used for Molecular Dynamics, where the force is not related to velocity. However, in DPD, F_{ij}^D does have a velocity component. Therefore a modification must be used. The simplest and effective fix is to merely recalculate F_{ij}^D at the end of the integration, before cycling back to the mid-step velocity calculation. This prescription was first developed by Besold *et al.* [145] and has been coined the DPD Velocity Verlet (DPD-VV) integrator.



A flow chart for the integration cycle:

A mid-step velocity is necessary in the cycle to reduce errors created in the equations of

motion. To get $\boldsymbol{r}_i(t+\Delta t)$, we need to look at the Taylor expansion.

$$\boldsymbol{r}_i(t + \Delta t) = \boldsymbol{r}_i(t) + \Delta t \boldsymbol{v}_i(t) + \frac{1}{2} \Delta t^2 \boldsymbol{a}(t) + \dots$$
(81)

Using this method causes numerical errors due to having a Δt^2 term. We can take this term out by using a mid step velocity. The Taylor expansion of v and a give us tools to do this.

$$\boldsymbol{v}_i(t + \Delta t) = \boldsymbol{v}_i(t) + \Delta t \boldsymbol{a}_i(t) + \frac{1}{2} \Delta t^2 \boldsymbol{b}(t) + \dots$$
(82)

$$\boldsymbol{a}_i(t + \Delta t) = \boldsymbol{a}_i(t) + \Delta t \boldsymbol{b}_i(t) + \dots$$
(83)

By rearranging equation (82), it can be seen that equation (83) can be substituted in to give equation (84)

$$\boldsymbol{v}_i(t+\Delta t) = \boldsymbol{v}_i(t) + \frac{1}{2}\Delta t[\boldsymbol{a}_i(t) + \boldsymbol{a}_i(t+\Delta t)]$$
(84)

Equation (84) can then be split into the mid-step and final velocity.

$$\boldsymbol{v}_i(t+\Delta t) = \boldsymbol{v}_i(t+\frac{1}{2}\Delta t) + \frac{1}{2}\Delta t\boldsymbol{a}_i(t+\Delta t)$$
(85)

where
$$\boldsymbol{v}_i(t + \frac{1}{2}\Delta t) = \boldsymbol{v}_i(t) + \frac{1}{2}\Delta t \boldsymbol{a}_i(t)$$
 (86)

Now the mid step velocity can be put into equation (81) to remove the Δt^2 term, as seen in equation (79).

Fluid Particle Model

Standard DPD only describes the solvent particles and so the model must be adapted to study a colloidal suspension. There are two main paths to modelling colloidal particles in DPD. One is to simulate the colloidal particle as a collection of DPD particles frozen together. Different variations of this path have been explored in the literature [130, 134– 136]. A setback for this way of simulating the colloid is the computational cost. A colloid is much larger than that of solvent particles and so we would be required to bond around 500 DPD particles together to create a single average colloid [138]. This would mean a fairly small system with 50 colloids would need 25,000 particles for the colloids alone. It can be seen that once the solvent is added to the system, there would be a significant number of particles that would be very computationally expensive to simulate.

The second method is to simulate the colloidal particle as a single large particle. The aim is to formulate a modification to the DPD force calculation which would allow for the approximation of a colloid as a single large free-moving sphere, surrounded by DPD solvent particles. This would greatly reduce the number of particles required in the simulation and therefore a more efficient model. The interparticle force from the standard form of the DPD framework does not allow for a single large sphere to impart the correct hydrodynamic interactions to the solvent particles due to the vast size disparity between the two types of particle [137–139]. Therefore, a modification to the framework is required to add rotational degrees of freedom between the colloidal particles and solvents. This torque is used to calculate the non-central shear acting on the binary system. One methodology to introduce the non-central shear forces into the DPD framework is the Fluid Particle Model (FPM) by Español [137]. To impart shear forces between two different sized particles, we require the angular momentum and velocity of the particles. The angular momentum was not previously required in the standard DPD method to calculate the shear, as the intrinsic angular momentum of each molecule would go to zero as the system is so large in comparison to one DPD particle [137]. However, now we would require the finite value of angular momentum for the larger colloid particle and collection of solvent molecules (the DPD particle) to correctly impart shear forces in the binary system.

The equations of motion, now become

$$\delta \boldsymbol{r}_i = \boldsymbol{v}_i \delta t \tag{87}$$

$$\delta \boldsymbol{v}_i = \frac{\boldsymbol{F}_i(t)}{m_i} \delta t \tag{88}$$

$$\delta \boldsymbol{\omega}_i = \frac{1}{I} \sum_{j \neq i} \boldsymbol{T}_{ij} \delta t \tag{89}$$

where $\boldsymbol{\omega}_i$, I and \boldsymbol{T}_{ij} are the angular velocity of particle i, the moment of inertia, and the torque experienced by particle i due to particle j, respectively. The torque is given by

$$\boldsymbol{T}_{ij} = -\frac{1}{2} \boldsymbol{r}_{ij} \times \boldsymbol{F}_{ij} \tag{90}$$

The propagation of the system is implemented the same as for standard DPD with the addition of the propagation of the angular velocity. This is done in the same way as translational velocity but with the torque instead of force and inertia of the particle instead of the mass.

$$\boldsymbol{\omega}_{i}(t+\frac{1}{2}\Delta t) = \boldsymbol{\omega}_{i}(t) + \frac{1}{2}\Delta t \frac{\boldsymbol{T}_{i}(t)}{I_{i}}$$
(91)

$$\boldsymbol{\omega}_{i}(t+\Delta t) = \boldsymbol{\omega}_{i}(t+\frac{1}{2}\Delta t) + \frac{1}{2}\Delta t \frac{\boldsymbol{T}_{i}(t+\Delta t)}{I_{i}}$$
(92)

The inclusion of angular momentum was achieved by splitting the dissipative force (\mathbf{F}_{ij}^D) into the translational (\mathbf{F}_{ij}^T) and rotational (\mathbf{F}_{ij}^R) forces.

$$\boldsymbol{F}_{i} = \sum_{j \neq i} \left(\boldsymbol{F}_{ij}^{C} + \boldsymbol{F}_{ij}^{T} + \boldsymbol{F}_{ij}^{R} + \widetilde{\boldsymbol{F}}_{ij} \right)$$
(93)

The conservative force (\mathbf{F}_{ij}^{C}) is derived from the potentials used for the pairwise interactions. For the interaction between two solvent particles, the standard DPD soft potential is used, as the solvents are soft particles. For the interaction between two colloid particles, a different potential is required to simulate the properties of the colloid. In this case, we have used the generalised Lennard-Jones potential to maintain the same colloidal interactions as the previous work within this thesis. However, the potential can be adjusted and changed to our liking depending on the type of system we would want to study in the future. The colloid-solvent interaction is modelled using the generalised Lennard-Jones potential but with the required changes to the parameters used due to the size and energy difference in the particles. Although the solvent particles can pass through each other using the soft potential, the repulsive characteristics the colloid particle take precedence to simulate the interactions correctly between the colloid and solvent particles. The potentials have the form,

$$U_{r_{ij}}^{cc} = \begin{cases} 4\epsilon_{cc} \left[\left(\frac{\sigma_{cc}}{r_{ij}} \right)^{2n} - \left(\frac{\sigma_{cc}}{r_{ij}} \right)^{n} \right], \text{ if } r_{ij} < r_{cc} \\ 0, \qquad \qquad \text{if } r_{ij} \ge r_{cc} \end{cases}$$
(94)

$$U_{r_{ij}}^{cs} = \begin{cases} 4\epsilon_{cs} \left[\left(\frac{\sigma_{cs}}{r_{ij}} \right)^{2n} - \left(\frac{\sigma_{cs}}{r_{ij}} \right)^{n} \right], & \text{if } r_{ij} < r_{cs} \\ 0, & \text{if } r_{ij} \ge r_{cs} \end{cases}$$
(95)

$$U_{r_{ij}}^{ss} = \begin{cases} \frac{1}{2} a_{ij} r_{ss} (1 - \frac{r_{ij}}{r_{ss}})^2, & \text{if } r_{ij} < r_{ss} \\ 0, & \text{if } r_{ij} \ge r_{ss} \end{cases}$$
(96)

The generalised Lennard-Jones potential is given, where n is varied depending on the desired range of the potential. r_{cc} , r_{cs} and r_{ss} are the cut-off distances for the interactions, where the subscript cc indicates a colloid-colloid, ss a solvent-solvent, and cs a colloid-solvent interaction.

The conservative force is derived from these potentials

$$\boldsymbol{F}_{cc}^{C}(\boldsymbol{r}_{ij}) = \begin{cases} \frac{4n\epsilon_{cc}}{r_{ij}} \left[2\left(\frac{\sigma_{cc}}{r_{ij}}\right)^{2n} - \left(\frac{\sigma_{cc}}{r_{ij}}\right)^{n} \right] \hat{\boldsymbol{r}}_{ij}, & \text{if } r_{ij} < r_{cc} \\ 0, & \text{if } r_{ij} \ge r_{cc} \end{cases}$$
(98)

$$\boldsymbol{F}_{cs}^{C}(\boldsymbol{r}_{ij}) = \begin{cases} \frac{4n\epsilon_{cs}}{r_{ij}} \left[2\left(\frac{\sigma_{cs}}{r_{ij}}\right)^{2n} - \left(\frac{\sigma_{cs}}{r_{ij}}\right)^{n} \right] \hat{\boldsymbol{r}}_{ij}, \text{ if } r_{ij} < r_{cs} \\ 0, & \text{if } r_{ij} \ge r_{cs} \end{cases}$$
(99)

$$\boldsymbol{F}_{ss}^{C}(\boldsymbol{r}_{ij}) = a_{ij} \left(1 - \frac{r_{ij}}{r_{ss}}\right) \hat{\boldsymbol{r}}_{ij}$$
(100)

The dissipative force is split into the translational and rotational forces with the random force adjusted accordingly to remain true to the fluctuation-dissipation theorem. The translational force equates the force of friction by relating the translational velocities with the vector positions and velocities.

$$\boldsymbol{F}_{ij}^{T} = -\gamma m \boldsymbol{M}^{T}(\boldsymbol{r}_{ij}) \cdot \boldsymbol{v}_{ij}$$
(101)

where $\boldsymbol{M}^{T}(\boldsymbol{r}_{ij})$ is in the form,

$$\boldsymbol{M}^{T}(\boldsymbol{r}_{ij}) = \left[f(r)\right]^{2} \boldsymbol{I} + \left[f(r)\right]^{2} \hat{\boldsymbol{r}}_{ij} \hat{\boldsymbol{r}}_{ij}$$
(102)

When this formulation is expanded, it is seen that we get the standard DPD equation for the dissipative force and an extra shear consideration.

$$\boldsymbol{F}_{ij}^{T} = -\gamma m \big[f(r) \big]^{2} \Big(\hat{\boldsymbol{r}}_{ij} \cdot \boldsymbol{v}_{ij} \Big) \hat{\boldsymbol{r}}_{ij} - \gamma m \big[f(r) \big]^{2} \boldsymbol{v}_{ij}$$
(103)

The rotational force is essentially the same as the translational force, but the velocity is replaced with the relative velocity at the surface of the particles. Here, FPM assumes the spheres i and j have radii of $r_{ij}/2$, are in contact, and are spinning with angular velocities $(\boldsymbol{\omega}_i \text{ and } \boldsymbol{\omega}_j)$ and no translational velocities. In this scenario, the relative velocity at the surface of these spheres is given as $\frac{1}{2}\boldsymbol{r}_{ij} \times (\boldsymbol{\omega}_i + \boldsymbol{\omega}_j)$. Therefore the rotational force is given as,

$$\boldsymbol{F}_{ij}^{R} = -\gamma m \boldsymbol{M}^{R}(\boldsymbol{r}_{ij}) \left(\frac{1}{2} \boldsymbol{r}_{ij} \times \left[\boldsymbol{\omega}_{i} + \boldsymbol{\omega}_{j} \right] \right)$$
(104)

where $M^{R}(\mathbf{r}_{ij})$ is in the same form as $M^{T}(\mathbf{r}_{ij})$. However, as the cross product in the calculation of the relative velocity at the surface of these spheres is perpendicular to $\hat{\mathbf{r}}_{ij}$, the second term is zero, and therefore the rotational force can be written,

$$\boldsymbol{F}_{ij}^{R} = -\gamma m \left[f(r) \right]^{2} \left(\frac{1}{2} \boldsymbol{r}_{ij} \times \left[\boldsymbol{\omega}_{i} + \boldsymbol{\omega}_{j} \right] \right)$$
(105)

The random force has been modified to match the changes in the dissipative force. This is because the random force must be able to balance the dissipation according to the fluctuation-dissipation theorem [137]. Español [137] deduced the random force to have the form,

$$\widetilde{F}_{ij}dt = \widetilde{\sigma}m \left(\widetilde{A}(r_{ij})\overline{dW}_{ij}^S + \widetilde{B}(r_{ij})\frac{1}{D}tr\left[dW_{ij}\right] + \widetilde{C}(r_{ij})dW_{ij}^A\right)\hat{r}_{ij}$$
(106)

where $\tilde{\sigma}$ is the strength of the random force with the form $\tilde{\sigma} = \sqrt{2\gamma k_B T}$, $\tilde{A}(r_{ij})$, $\tilde{B}(r_{ij})$ and $\tilde{C}(r_{ij})$ are scalar functions, and \overline{dW}_{ij}^S , dW_{ij}^A and $tr\left[dW_{ij}\right]$ are the traceless symmetric, anti-symmetric and trace random matrices, respectively. The random matrices follow these rules,

$$d\boldsymbol{W}_{ij}^{S\mu\nu} = \frac{1}{2} \Big[d\boldsymbol{W}_{ij}^{\mu\nu} + d\boldsymbol{W}_{ij}^{\nu\mu} \Big], \qquad (107)$$

$$d\boldsymbol{W}_{ij}^{A\mu\nu} = \frac{1}{2} \Big[d\boldsymbol{W}_{ij}^{\mu\nu} - d\boldsymbol{W}_{ij}^{\nu\mu} \Big], \qquad (108)$$

$$\overline{d\boldsymbol{W}}_{ij}^{S} = d\boldsymbol{W}_{ij}^{S} - \frac{1}{D}tr\Big[d\boldsymbol{W}_{ij}^{S}\Big].$$
(109)

where D is the number of physical dimensions of the system and $d \pmb{W}_{ij}^{\mu\nu}$ is a matrix of inde-

pendent Gaussian random numbers with zero mean and unit variance. Due to momentum conservation, $dW_{ij}^{\mu\nu} = dW_{ji}^{\mu\nu}$ to ensure that $\tilde{F}_{ij} = -\tilde{F}_{ji}$.

It is common practice to set $\tilde{A}(r_{ij}) = 0$, $\tilde{B}(r_{ij}) = \sqrt{2D}[f(r)]$ and $\tilde{C}(r_{ij}) = \sqrt{2}[f(r)]$ [137–139]. By putting these into equation (106) we can get our functional form of the random force.

$$\widetilde{\boldsymbol{F}}_{ij}dt = \widetilde{\boldsymbol{\sigma}}\left[f(r)\right] \left[\frac{\sqrt{2D}}{D} tr\left[d\boldsymbol{W}_{ij}^{S}\right]\boldsymbol{I} + \sqrt{2}d\boldsymbol{W}_{ij}^{A}\right] \cdot \hat{\boldsymbol{r}}_{ij}$$
(110)

Pryamitsyn and Ganesan [138] have developed a variation to the Fluid Particle Model by adding a prefactor, λ_{ij} , which would weight the force according to the size difference between the colloid and solvent. This λ_{ij} prefactor dictates the ratio between the two spheres that are interacting in each pairwise interaction.

$$\lambda_{ij} = \frac{R_i}{R_i + R_j} \tag{111}$$

For the solvent-solvent and colloid-colloid interactions the prefactor would merely by 1/2, and so the standard FPM model is observed. For the systems we desire to simulate the colloid would be much bigger that the solvent DPD particles and so the prefactor would heavily weight the forces toward the colloid in the case of a colloid-solvent interaction. The work by Pryamitsyn and Ganesan [138] was a small change, but effective in modelling the colloid as a single-particle, with dynamics and rheological behaviour being correctly simulated for simple fluid solvents. The torque is written as,

$$\boldsymbol{T}_{ij} = -\lambda_{ij} \boldsymbol{r}_{ij} \times \boldsymbol{F}_{ij} \tag{112}$$

The rotational force is now given the form,

$$\boldsymbol{F_{ij}^R} = -\gamma m \big[f(r) \big]^2 \Big(\boldsymbol{r}_{ij} \times \big[\lambda_{ij} \boldsymbol{\omega}_i + \lambda_{ij} \boldsymbol{\omega}_j \big] \Big)$$
(113)

Benchmarking

Benchmarking the standard DPD framework

As with the Brownian Dynamics framework developed for this thesis, we must benchmark the code in order to be confident in the data that is produced for new systems.

Figure 51 shows the static and dynamic properties of the system comparing the radial distribution function (static) and the velocity auto-correlation function (dynamic) from our framework and that reported by Leimkuhler and Shang [148, 149]. The match is near perfect at all timesteps with the only discrepancy at the near zero distance for the radial distribution function at a timestep of $\Delta t = 0.13\tau$. This discrepancy is purely down to the width of the shells used in the process of calculating the radial distribution function.

Another benchmarking method is to look at the diffusion coefficients we obtain from the simulation and see if they match with the literature [150]. The diffusion coefficient is a good benchmarking tool, as it can be calculated from two separate outputs from the



(a) Radial distribution function from the in-house framework



(c) Velocity auto-correlation function from the in-house framework



(b) Radial distribution function taken from Ref 148



(d) Velocity auto-correlation function taken from Ref 148

Figure 51: Radial distribution function and velocity auto-correlation of a system of 500 solvent DPD particles at a reduced number density of $\rho^* = 4.0$. The strength of the interaction was set to $a_{ij} = 25\epsilon$ and the strength of the dissipative force to $\gamma = 4.5\epsilon$. The parameters followed from the literature we are benchmarking against [148]. (b)+(c) images taken from Ref 148. The comparison of the plot show how the in-house framework gives concordant results to the literature. In our our work Δt is the timestep used in each simulation, which mirrors the timesteps given in the literature labelled as h.

system. One method is to use the mean square displacement (MSD) of the particles in the system, described in chapter 2.

Figure 52 shows the plot of MSD against time for our solvent-only DPD system with the dissipative strength, $\gamma = 4.5\epsilon$. The gradient of the plot is 1.8213, so with the simulation being in three dimensions, $6D = 1.8213\sigma^2/\tau$ we obtain the diffusion coefficient, $D = 0.30355\sigma^2/\tau$. This matches with the literature, where Chaudhri and Lukes [150] reports

a value of around $0.3\sigma^2/\tau$ for the diffusion coefficient.



Figure 52: The mean-squared displacement against time of a 3000 particle system at a reduced number density of $\rho^* = 3.0$, following the parameters give by the literature [150]. The gradient of this plot is used to calculate the diffusion coefficient. The calculated diffusion coefficient matches with literature [150].

The other method of calculating the diffusion coefficient is via the Green-Kubo relation of the velocity auto correlation function [151–153]. In the same way that the stress auto correlation function can give information on the equilibrium viscosity of the system, the VACF can give information on the diffusion of the system, the relation is seen in equation (114). The value for the diffusion coefficient measured in this way matches well with the MSD data and also to the literature [150].

$$D = \frac{1}{N} \int_0^\infty \left\langle v_i(t) v_i(0) \right\rangle dt \tag{114}$$

To further benchmark the solvent-only DPD code, we employed the external package that was used by Leimkuhler and Shang [148] in their study. By using the external package directly we can guarantee that our framework is working as intended. This external package is DL_MESO. DL_MESO is capable of utilising a whole host of different integrators and boundary conditions, along with several utility packages for analysis, including the DPD-VV integrator and Lees-Edwards shearing boundary. This program is great for initial benchmarking of the system, but we still chose to develop our own in-house code to allow us to manipulate the framework for novel systems we wish to study. The data we observed from the external packaged matched the values from our system and the literature. From this data we are confident that the framework developed in-house is working correctly for the initial solvent-only DPD system.

(DL_MESO is a mesoscale simulation package written by R. Qin, W. Smith and M. A. Seaton [154] and has been obtained from STFC's Daresbury Laboratory via the website http://www.ccp5.ac.uk/DL_MESO)

Benchmarking the Lees-Edwards shearing boundary

With the backbone of the code complete, we moved onto developing the Lees-Edwards shearing periodic boundary condition. This boundary condition will impart shear on the DPD system and allow us to study the phase behaviour and rheological properties. The system we are benchmarking is merely a Newtonian solvent, but we will need this dynamic capability to study colloidal systems.

To initially benchmark the shearing code, we need to calculate the viscosity of the system

under shear, i.e. the shear viscosity.

$$\eta_{\alpha\beta}^* = \frac{\sigma_{\alpha\beta}}{\dot{\gamma}} \tag{115}$$

Viscosity is calculated according to equation (115), where $\dot{\gamma}$ is the shear rate and $\sigma_{\alpha\beta}$ is the shear stress. Unlike in the Brownian Dynamics framework that is in the overdamped limit, the particle velocities are tracked in the DPD framework and so we must include the kinetic term of the Irving-Kirkwood stress tensor, the full tensor is given in equation (116),

$$\sigma_{\alpha\beta} = -\frac{1}{V} \left[\sum_{i=1}^{N_p} m_i(\boldsymbol{v}_{i\alpha} \boldsymbol{v}_{i\beta}) + \sum_{i=1}^{N_p} \sum_{j>i}^{N_p} \boldsymbol{r}_{ij,\alpha} \cdot \boldsymbol{F}_{ij,\beta} \right]$$
(116)

The stress calculation itself must be benchmarked to use the viscosity data that comes from it. To do this, we can look at the stress auto-correlation function (SACF) in conjunction with equipartition theory [147, 150]. Due to equipartition the average kinetic energy from the translational degrees of freedom is equal to $\frac{1}{2}mv^2$ and also equal to $\frac{3}{2}k_BT$. At low friction, the kinetic term of the stress calculation is dominant [150], therefore, $\sigma_{xx} = \frac{1}{V} \sum_{i=1}^{N_p} m_i(\boldsymbol{v}_{ix}\boldsymbol{v}_{ix})$. In turn, $\langle \sigma_{xx}(0)\sigma_{xx}(0)\rangle = \frac{N_p}{V}(mv^2)$. $\frac{N_p}{V}$ is simply the density of the system and, following equipartition, mv^2 can be written as $3k_BT$, meaning that $\langle \sigma_{xx}(0)\sigma_{xx}(0)\rangle = 3\rho k_BT$. The system parameters used are $\rho^* = 3$ and $T^* = 1$, therefore, we should expect in our simulation that $\langle \sigma_{xx}(0)\sigma_{xx}(0)\rangle = 9$. The value of 9 is indeed observed with our SACF calculation confirming the benchmarking for the stress calculation in our framework.

We can also calculate the equilibrium viscosity of the system through the Green-Kubo relation with the SACF. This is discussed in chapter 2. The reported value is around

 $1\epsilon/\sigma D_0$ [150, 155], however, with the fluctuation in stress at equilibrium being quite large and the heavily statistical nature of the calculation we won't be expecting a perfect match in values [155]. Following the key system parameters set out in Ref 150 (seen in table 66.2), we observe a viscosity of $1.0178\epsilon/\sigma D_0$ from our program, confirming that the code is correctly calculating stress. The calculated viscosity fluctuated when using different values of Δt , but we believe the fluctuation is within tolerance to be confident in the framework.

Parameter	Description	Value
N	Number of particles	3000
V	Volume	$1000\sigma^3$
$ ho^*$	Reduced Density	3.0
r_{cut}	Cut-off Radius	1.0σ
T^*	Reduced Temperature	1.0
γ	Drag strength	4.5ϵ
a_{ij}	Interaction strength	10.0ϵ
Δt	Timestep	0.04τ

Having first benchmarked the standard DPD system with stress calculations, we can now calculate the shear viscosity and benchmark the shearing boundary condition. The system we are simulating is made up solely of solvent particles, the system should act as a Newtonian liquid [156], this means that the viscosity should remain constant as a function of the rate of shear applied to the system. Checking whether our code gives a constant viscosity will tell us whether the periodic shear boundary is working correctly. We used the dissipative rate of $\gamma = 4.5\epsilon$, where our shear viscosity was well matched to

the literature, to calculate the viscosities at a range of shear rates. It was observed that the shear viscosity remains constant at around $0.87\epsilon/\sigma D_0$ through all shear rates, as seen in Figure 53.



Figure 53: A plot which shows the shear viscosity of the system at different shear rate. The observed constant trend helps to prove that the shear is correctly being imparted on a Newtonian solvent.

Initial benchmarking of the FPM framework

Due to time constraints, the FPM framework was only partially developed with very basic initial benchmarking completed. It will be vital to the future study of dynamic systems to complete the development of this explicit solvent technique.