Improved Models of Colloidal Gels: Kinetic Arrest, Relaxation Dynamics, Structural Breakdown and the Role of Hydrodynamic Interactions

by

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Submitted to the Department of Chemical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY June 2018

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Abstract

Colloidal gels, composed of sub-micron, mutually attractive particles that aggregate to form a system spanning network, are the most abundant and diverse soft matter in society with numerous familiar, yet also many exotic applications, ranging from common dairy products to novel medical implants. Despite this profusion, the link between network microstructure and macroscopic behavior and function remains a mystery. Computational models of the microstructural evolution of colloidal gels present one opportunity to efficiently study the emergence of bulk material properties. However, these simulations often fail to match experimental results and are unable to reproduce landmark observations set as benchmarks. This thesis is concerned with the systematic study of the influence of hydrodynamic interactions on colloidal gelation to explain the prevailing experimental-theoretical mismatch in the literature. The novel insights drive the development of improved models that can accurately describe the physics of colloidal gels.

A series of computational studies carefully investigate the role of hydrodynamic interactions in determining the conditions for kinetic arrest of attractive dispersions. The collective dynamics enabled by fluid mechanics are shown to enhance coagulation leading to a shift in the gel boundary to lower strengths of attraction and lower particle concentrations when compared to models that neglect hydrodynamic forces. Simulations with long-ranged hydrodynamic interactions are found to faithfully reproduce experimental phase diagrams. This is shown to hold true both for purely attractive dispersions as well as in systems with repulsive barriers. Perturbation analysis is used to study the rheology of semi-dilute, attractive colloidal dispersions and it is demonstrated that both hydrodynamic interactions and the interparticle potential critically affect the viscoelasticity of the material. A normal mode analysis on colloidal gels is conducted using different models of the hydrodynamic interactions between suspended particles to investigate the relaxation rates and energy dissipation in the network. It is established that computational models neglecting long-ranged hydrodynamic interactions critically fail to compute accurate values of rheological properties of interest.
These findings are then integrated to study experimentally observed instabilities of attractive dispersions under shear and during sedimentation. Models accounting for the prevalent hydrodynamic forces are used to demonstrate that the phenomena of vorticity alignment and log-rolling are fluid mechanical in origin. Experimental measurements of density fluctuations and shear anisotropy are accurately recovered in simulations for the first time. Finally, a theory is developed to quantitatively predict the collapse dynamics of freely settling colloidal gels and new engineering strategies for extending the process lifetime of gel networks are presented. The observations and results discussed in this thesis leave no doubt that the properties and the mechanical response of gels are fundamentally altered by many-body hydrodynamics. These will have to be properly accounted for in the first generation of predictive computational models employed in the engineering design of colloidal gels.

Thesis Supervisor: James W. Swan
Title: Texaco-Mangelsdorf Career Development Professor in Chemical Engineering
Családomnak,
öten a világ ellen.
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Köszönöm.
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Chapter 1

Introduction

Dispersions of colloids, sub-micron sized particles suspended in a viscous fluid, are a prevalent type of soft material with enormous technological significance used in a wide variety of products including paints, coatings, ceramics, mineral processing, foodstuffs, pharmaceuticals, and personal care [1–3]. More recently, colloidal dispersions have been employed in emerging technological application such as for drug delivery and medical implants or for catalysis and in the development of nanostructured materials [4–6].

In the possibly simplest colloidal dispersion of hard spheres, particles only interact with each other through a hard core excluded volume interaction, the equilibrium states are determined solely from the entropy as a function of the particle volume fraction. Such near hard sphere behavior has even been achieved in real dispersions [7]. However, one of the most promising aspects of colloidal dispersions making them interesting to many applications, is the ability to tune the interparticle interactions. These have been shown to directly influence the structure and dynamics at the microscale as well as the overall macroscopic properties of the dispersion [8]. The dispersions exhibit a wide variety of phase transitions and mechanical behavior that is far more complex than for simple, one-component fluids [9].

With the introduction of an attractive potential, thermodynamic equilibrium is dictated by the internal energy and entropy of the system. For a large range of particle volume fractions and interaction strengths, thermodynamic theory predicts the stability of different co-existing phases, e.g. dense colloidal crystals in a dilute fluid [10]. However, upon thermodynamic instability, the mechanism of phase separation is controlled by physical transport
processes and dispersions with sufficient interparticle attraction can reach a state of dynamic arrest instead, away from energetic equilibrium. Attractions between particles promote the growth of aggregates that coagulate to form a physical gel—a slowly aging, sample-spanning network [9].

The percolated structure imparts solid-like elasticity and other macroscopic material properties making gels attractive for a diverse range of applications. Colloidal gels have been used to construct biodegradable artificial tissue and for scaffolds that engender cell growth in vivo [11], they are are extensively studied for suitability as pharmaceutical vehicles [12] and are of interest in research on emulsions, proteins [13] and in cell biology [14]. Gelation is also ubiquitous in consumer goods processing, including the production of common dairy products and cosmetics [3, 15]. Careful control and intelligent design of particle gels is critical for several novel materials applications, in heterogeneous catalysis [16], optics, energy-harvesting [17], as LEDs and thermo-electrics [18] or as catalytic electrodes in fuel cells [19].

Despite their abundance in society, optimizing the final mechanical properties of gels and more importantly, predicting the outcome of soft material processing has until now proven to be challenging. As colloidal gels are kinetically arrested and are far from thermodynamic equilibrium, their properties are highly sensitive to the methods by which the network is prepared [9, 20]. There now exists consensus that in order to predict and control the desired mechanical properties, it is important to understand the necessary conditions for gel formation and how the microstructure evolves post-gelation [21, 22]. However, even the location and origin of the gelation transition on a phase diagram are still the subject of considerable debate [9, 23–25]. Consequently, to date, there is no established, robust model predicting the final arrested microstructure and linking it to measured rheological properties, such as the modulus and the yield stress, or even the stable lifetime of a gel. A microscopically observable order parameter that relates to the emergence of bulk properties has not been identified experimentally. Furthermore, in experiments where these gels are subjected to external stresses, such as shear flow or gravitational instability, the path leading to, and mechanism of breakdown of the network microstructure often cannot be explained. A lack of theory describing the modes of failure can be prohibitive to the application of colloidal gels in many industries [26, 27]. The development of a systematic understanding of kinetically
arrested materials such as colloidal gels is therefore among the most important problems in soft matter science today.

Given the absence of comprehensive theories and numerous experimental limitations, particle-based dynamic simulations are an important tool in the study of attractive colloidal dispersions as protocols for the preparation of kinetically arrested phases are perfectly repeatable. A detailed computer simulation is able to provide particle level information with high temporal resolution and thus offers one promising means of discovering the desired connection between microscopic degrees of freedom and macroscopic responses and could elucidate how bulk mechanical properties emerge. Ideally, a model would produce accurate and reliable results of the structure and dynamics of arrested colloidal dispersions that could be linked to the resultant gels' mechanical and transport properties. These predictions could then be used for targeted material engineering design. The challenge in constructing this desired parsimonious model lies in striking a balance between the cost of the necessary computational complexity and an accurate representation of the relevant physical processes governing the behavior of colloidal gels.

In particular, in low-Reynolds-number flow each and every interaction in colloidal dispersions is mediated by the fluid surrounding the colloidal particles through hydrodynamic interactions, which can dramatically affect the dynamics of the embedded particles. It is well established that the fluid mechanics of attractive and repulsive dispersions determine the rheology of the material and fluid flow controls key mechanical descriptors such as the complex modulus [28]. There is thus a long standing question regarding the role of these hydrodynamic forces in determining the observed outcome of kinetic arrest [29]. These interactions are fundamentally long-ranged, which makes their mathematical description in theoretical and computational models problematic [30, 31]. While models can be constructed, which neglect the collective motion of hydrodynamically interacting particles, the gelation kinetics and gel microstructure depend on the dissipation mechanisms within the gel. As is discussed throughout this work, the coarsening, the rheological response, and the stability of colloidal gels at different ages exhibit a significant sensitivity to hydrodynamic interactions between particles. A useful parsimonious discrete element model of colloidal gels will therefore model these interactions accurately.
Thesis outline

The remainder of this thesis is organized as follows. Chapter 2 details the physical features relevant to the study of dispersion of colloidal particles. The hydrodynamic interactions in low-Reynolds-number flow of colloidal particles and the Langevin equation governing the stochastic motion of Brownian particles are presented. Then, the discrete element simulation methodology employed and the model system along with the interparticle potentials and approximations for the hydrodynamic mobility used to study colloidal gels are described. The remaining chapters discuss the behavior and response of colloidal dispersions under various physical conditions and highlight the critical role that hydrodynamic interactions play in these situations.

In chapter 3 simulations of gelation with and without hydrodynamic interactions between the suspended particles are compared. The large observed disparities between these approaches mirror the experimental-theoretical mismatch in the literature. It is shown that in order for computational predictions to agree with experimental observations, hydrodynamic forces have to be consequently accounted for in simulations. A simple model of the competing transport processes in gelation is explored that anticipates these disparities. Near the gel boundary, there exists a competition between compaction of individual aggregates which suppresses gelation and coagulation of aggregates which enhances it. The time scale for compaction is mildly slowed by hydrodynamic interactions, while the time scale for coagulation is greatly accelerated. This enhancement to coagulation leads to a shift in the gel boundary to lower strengths of attraction and lower particle concentrations when compared to models that neglect hydrodynamic interactions. It is argued that this requires a fundamental rethinking of which dynamic, discrete element models for gelation kinetics are employed as well as how collective hydrodynamic interactions influence the arrest of attractive colloidal dispersions.

Chapter 4 studies gelation in a dispersion of colloids interacting pair-wise via a short-ranged attraction and long-ranged repulsion and juxtaposes self-assembly with and without hydrodynamic interactions between the particles. The percolation boundaries predicted by simulations including hydrodynamic interactions are again found to agree well with those
measured experimentally in similar dispersions. The long-ranged repulsion impacts the relative rates of coagulation and compaction of colloidal aggregates pre-gel, and introduces an additional sensitivity to the nature of hydrodynamic interactions between the suspended colloids. Differences between the models, which persist far from the percolation boundary, are evidenced via measurements of the fractal dimension, local bond order parameters, and the collective relaxation dynamics. Notably, it is found that the growth of anisotropic clusters is augmented in simulations that incorporate long-ranged hydrodynamic interactions due to the anisotropic diffusion of elongated bodies at low-Reynolds-number flows. This favors percolation over a transition of anisotropic clusters to their more isotropic ground states. The chapter ends with a discussion about the necessity of incorporating long-ranged hydrodynamic forces in discrete element simulations of heterogeneous gelation at the colloidal scale.

Next, in chapter 5 the rheology of semi-dilute attractive colloidal dispersions preceding gelation is analyzed. The complex viscosity of these materials is calculated by investigating their response to weak oscillatory shear. A first order expansion in small rates of deformation is used to solve for the microstructure and stress in the dispersion. The effect of fluid mechanics is studied via a continuous variation of the hydrodynamic interaction strength. It is found that the viscoelastic response exhibits a sharp transition when going from weak to strong attractions. Below a critical strength, increasing the interparticle attraction reduces the low frequency viscosity. Strong attractions increase the viscous response and delay the onset of an elastic plateau at high frequencies. An asymptotic analysis is employed to show that the stress response is a result of the interplay of two length scales: the range of attraction and the diffusive boundary layer around particles. The complex viscosity is described with high accuracy by two well characterized viscoelastic models independent of the strength of hydrodynamic interactions: At low frequencies, a Maxwell mode; at high frequencies, the purely repulsive hard sphere response.

The normal modes and relaxation rates of colloidal gels in calculations using different models of the hydrodynamic interactions between the suspended particles are investigated in chapter 6. Through a normal mode analysis of a harmonic network representing colloidal gels the relaxation spectrum is computed for approximations of the hydrodynamic mobility.
with increasing complexity. The density of states and spatial structure of the normal modes are found to be fundamentally altered by long-ranged hydrodynamic coupling among the particles. Short-ranged coupling due to hydrodynamic lubrication affects only the relaxation rates of short wavelength modes. A simple phenomenological model of the internal elastic response to normal mode fluctuations is developed and dynamic simulations of gels are conducted to show the applicability of the normal mode analysis. The power law decay of the relaxation modulus in simulations agrees with both predictions generated by the density of states of the corresponding harmonic networks, and with experimental measurements.

Chapter 7 considers the structural breakdown and the resulting vorticity aligned density fluctuations exhibited by attractive colloidal dispersions under steady shear, measured in numerous experiments. Dynamic simulations are used to show that this instability is fluid mechanical in origin, and results from long-ranged hydrodynamic interactions, which stabilize the vorticity aligned flocs. Squeeze flows between flocs prevent collisions and realignment under flow, thus promoting stability of the large scale, density fluctuations. A single force scale – the most probable rupture force for the intercolloid bonds collapses the microstructural and rheological data across different strain rates and strengths of interaction. Two distinct regimes of the shear response critical to both computational and experimental studies are identified: dynamic yield and steady shear flow. The nonlinear rheology in sheared colloidal gels and measures of their structural anisotropy seen in simulations agree well with a variety of experiments and are independent of the regime of steady-state response. The relevant consequences for future computer simulations and experiments on sheared attractive dispersions are discussed to conclude the chapter.

The specific effect of confinement on attractive dispersions and the widely reported phenomenon of shear-induced structure formation is investigated in chapter 8. For the first time, vorticity aligned log-rolling is successfully reproduced in dynamic simulations. Measurements of the log sizes and of the characteristic spacing between them agree quantitatively with the experiments. A physical mechanism for shear-induced pattern formation is proposed that suggests a fluid mechanical origin. The superposition of planar Couette flow and flow between parallel plates as a result of a disturbance results in a set of periodically spaced hydrodynamic point torques co-rotating around stagnation points. These act as attractors
for the particle aggregates and are the only stable steady-state, as confirmed by further simulations employing modified initial states. This mechanism is able to consistently explain the observed characteristics and suggests intriguing opportunities for the targeted application of structuration to achieve tight size specifications of novel materials.

In chapter 9 a theory is developed for the hydrodynamic instability in freely settling colloidal gels leading to loss of network integrity. Experimental observations have shown that the loss of integrity is associated with the formation of eroded channels, so-called streamers, through which the fluid flows rapidly. A phenomenological model is presented that describes dynamically the radial growth of a streamer due to erosion of the network by rapid fluid back flow. The model exhibits a finite-time blowup – the onset of catastrophic failure in the gel – due to activated breaking of the intercolloid bonds. A set of dynamic simulations is employed to examine the initiation and propagation of this instability, which is in good agreement with the theory. The model dynamics are also shown to accurately replicate measurement and predict the dynamics of streamer growth in two different experimental systems. A stability-state diagram is presented and insight into new strategies for avoiding settling instabilities and rationally engineering long shelf lives are analyzed. The thesis concludes with a brief summary of the key results and a discussion of remaining open questions and future directions for this work.
Chapter 2

A Computer Model of Colloidal Scale Physics

A fully atomistic description of $N$ colloidal spheres in $N_s$ solvent molecules would require resolving $N + N_s$ equations of motion. However, it can be readily shown that the relevant length and time scales of solvent and colloidal particles are mismatched by several orders of magnitude [8]. Naively implemented, most of the computation time would be spent resolving the solvent dynamics when it is the colloidal dynamics that are desired. To achieve a reduction in complexity the solvent can be treated as a single, continuous medium.

2.1 Low-Reynolds-number hydrodynamics

The Navier-Stokes equations are the continuum equations governing the momentum of a Newtonian fluid. This thesis is concerned with low-Reynolds-number flows where in a fluid of density $\rho$ and viscosity $\eta$, the Reynolds number, $\text{Re} = ul/\eta$, is small with arbitrary length scale $l$ and velocity scale $u$. Consequently the viscous forces throughout the fluid are significantly stronger than inertial forces and the velocity $u$ and pressure $p$ of the fluid are
governed by the Stokes equations [32]:

\[ \nabla \cdot \mathbf{u} = 0, \quad (2.1) \]

\[ \nabla p = \eta_s \nabla^2 \mathbf{u}. \quad (2.2)\]

While in general the Stokes equations cannot be valid everywhere for an arbitrarily small, but finite Reynolds number, for the purposes of this work, the Reynolds number is identically zero over all length scales.

Because of the linearity of the Stokes equations, the resulting velocity field, its gradients and higher order derivatives are linear functions of the conditions at the boundary of the fluid. This has significant consequences for the dynamics of colloidal particles in a viscous fluid. Colloidal particles interact generically through the solvent via hydrodynamic interactions, which are determined by the viscous response of the fluid to motion of the immersed colloid boundaries, as described by the Stokes equations. These hydrodynamic interactions are long-ranged and decay with the inverse of the distance between suspended objects, which reflects the fundamental nature of the flow field induced by motion of colloidal objects in a viscous fluid. However, as a universal solution to the Stokes equations does not exist, in dynamic simulations the resulting hydrodynamic interactions influencing the slow viscous flow of colloids in the solvent have to be approximated, employing in general one of two techniques.

### 2.1.1 Approximations for hydrodynamic interactions

In one approach, instead of solving the momentum conservation equations directly, the motion and response of the solvent is determined explicitly, either by representing the solvent as a discrete collection of momentum carrying quasi-particles, or via discretization and replication of solutions of the Stokes equations around the particles. The most common of these are Lattice Boltzmann [33], Stochastic Rotation Dynamics [34], Multi-Particle Collision Dynamics [35], and Dissipative Particle Dynamics [36]. While the computational cost of calculating hydrodynamic interactions is linear in the number of particles, these algorithms are limited by the need to resolve inertial degrees of freedom in the solvent. This results in a significant
loss of efficiency on approach to overdamped systems, requiring careful control of relevant
dimensionless groups and makes these methods very costly for large scale simulations [37].

Alternatively, the motion of the solvent can be represented implicitly, the approach
adopted also in this work. Deterministic and stochastic forces acting directly on the col-
loidal particles are used to determine the particle trajectories. The additional particle mo-
tion induced by hydrodynamic interactions is constructed from multipolar expansions of the
fundamental solutions of the Stokes equations. Using a Green’s function formulation for
Stokes flow it is possible to arrive at a grand mobility tensor, $\mathcal{M}$ that linearly couples all the
moments of the hydrodynamic force density (the force, $F^H$; the torque, $L^H$; the stresslet,
$S^H$; etc.) on the rigid colloid surfaces to the moments of the particle velocities (translational,
$U$; rotational, $\Omega$; etc.) in a stationary ambient field [32]:

$$
\begin{pmatrix}
    U \\
    \Omega \\
    0 \\
    \vdots
\end{pmatrix} =
-\begin{pmatrix}
    M_{UF} & M_{UL} & M_{US} & \cdots \\
    M_{GF} & M_{GL} & M_{GS} & \cdots \\
    M_{EF} & M_{EL} & M_{ES} & \cdots \\
    \vdots & \vdots & \vdots & \ddots
\end{pmatrix} \cdot
\begin{pmatrix}
    F^H \\
    L^H \\
    S^H \\
    \vdots
\end{pmatrix}
$$

(2.3)

As discussed in section 2.3, different implicit simulation methods differ based on the level
of accuracy and order of the multipole expansion to which hydrodynamic interactions are
approximated.

Throughout the majority of this manuscript, the rotational velocity, the torque and the
stresslet will be neglected and dynamic simulations will only consider the zeroth moment of
the hydrodynamic force density, the hydrodynamic force, $F^H$, itself. As a result, the element
of $\mathcal{M}$ coupling the hydrodynamic force on the particles linearly to the particle velocities,
$M_{UF}$, will consistently be denoted $M$:

$$
U = -M_{UF} \cdot F^H = -M \cdot F^H.
$$

(2.4)

When higher moments are considered and included in simulations, this will be clearly stated
and the notation of the elements of the grand mobility tensor will be adjusted accordingly.
2.2 The Langevin equation

In a continuum solvent, the trajectory of each of the $N$ particles in the dispersion satisfies the stochastic Langevin equation [38]:

$$\frac{dU}{dt} = F^H + F^B + F^P,$$  \hspace{1cm} (2.5)

where $m$ is the mass of the particles, and the force vectors include the deterministic hydrodynamic force, $F^H$, a stochastic Brownian force, $F^B$, and a deterministic nonhydrodynamic force, $F^P$, originating from the negative gradient of interparticle interactions or from external forces.

The characteristic time scale for momentum relaxation of a particle of size $a$ in a solvent of viscosity $\eta_s$ is $\tau_I = m/6\pi\eta_s a$. For colloidal scale particles with radius $1\mu m$ in water, this is typically on the order of $10^{-7}s$ and far shorter than the time scales of interest. The particles themselves move on the characteristic time scale for diffusion:

$$\tau_D = 6\pi\eta_s a^3/kT,$$  \hspace{1cm} (2.6)

which is typically on the order of $1 - 10s$ for the same particles. Here $k$ is the Boltzmann constant, $T$ is the solvent temperature. The ratio: $Sc= \tau_D/\tau_I$, is called the Schmidt number and describes the relative importance of momentum relaxation and diffusive transport. For a typical colloidal scale particle the Schmidt number is on the order of $10^8$, indicating that any change to the particle's momentum occurs effectively instantaneously, the inertial term in (2.5) can be neglected. In the absence of the effect of inertia, the equations of motion are completely mass-independent, i.e. overdamped:

$$0 = F^H + F^B + F^P.$$  \hspace{1cm} (2.7)

Substituting for the hydrodynamic force and rearranging results in a stochastic differential
equation for the particle trajectories:

\[
\frac{dx(t)}{dt} = M \left( F^B + F^P \right),
\]

(2.8)

where \( x(t) \in \mathbb{R}^{3N} \) is the position vector of the particles at time \( t \). Discretizing (2.8) in time with the Euler-Maruyama integrator yields a discrete displacement equation with \( O(\Delta t) \) accuracy [39]:

\[
x(t + \Delta t) = x(t) + M \cdot F^P \Delta t + kT \nabla \cdot M \Delta t + \Delta x^B(t).
\]

(2.9)

Here, \( \Delta x^B(t) \) is the stochastic displacement vector as a result of the instantaneous Brownian force \( F^B \). The statistics of Brownian motion and the model implementations for the interparticle forces are discussed next.

### 2.2.1 Brownian motion

In the continuum mechanics approach, to account for the Brownian motion of the suspended particles, a fluctuating stress acting on the fluid must be incorporated into the momentum balance. On time scales that are long relative to the momentum relaxation time of the solvent, this stochastic stress has an equivalent representation as an instantaneously correlated stochastic force, \( F^B \), acting directly on the particles. The Brownian force satisfies the fluctuation-dissipation theorem and the mean value and the autocorrelation are characterized by [8]:

\[
\left\langle F^B(t) \right\rangle = 0,
\]

(2.10)

\[
\left\langle F^B(t)F^B(0) \right\rangle = 2kT M^{-1} \delta(t),
\]

(2.11)
where $\delta(t)$ is the Dirac delta function. Equivalently, the Brownian displacement in the discretized, overdamped Langevin equation obeys:

\[
\begin{align*}
\langle \mathbf{x}^B(t) \rangle &= 0, \\
\langle \mathbf{x}^B(t) \mathbf{x}^B(t) \rangle &= 2kT M \delta(t) \Delta t.
\end{align*}
\] (2.12) (2.13)

The stochastic Brownian forces depend on the position of the particles through the mobility tensor and computation of the Brownian displacement necessitates the computation of the action of the square root of the mobility on a vector. This step represent the most time-consuming calculation in an implicit dynamic simulation of Brownian particles.

### 2.2.2 Interparticle interactions

As discussed in the previous chapter, a wide variety of the observed phenomena in colloidal disperisons is attributed to the interparticle interactions in the presence of hydrodynamic interactions and Brownian motion. In this work, the interparticle interactions are consistently approximated by pair-wise potentials of the form $U(r)$, where $r = |\mathbf{r}|$ is the magnitude of the center-to-center vector, $\mathbf{r}$, between two particles. The resulting central force between particles is obtained as the negative gradient of the potential.

**Hard sphere potential**

Regardless of any other interactions, the colloidal particles of radius $a$ are modeled as rigid hard spheres that cannot overlap and as such experience hard repulsion at contact, but are otherwise noninteracting:

\[
U(r) = \begin{cases} 
\infty & r < 2a \\
0 & r \geq 2a.
\end{cases}
\] (2.14)

The discontinuity in this potential, however, makes it difficult to directly incorporate into simulations. Traditionally, MD simulations employ the Weeks-Chandler-Anderson soft potential to approximate hard repulsion [40]. However, the potential introduces some softness, allows for the overlap of particles and can generate unphysically large forces. This can be
problematic when the particle system is driven out of equilibrium by flow, scenarios that are investigated in this thesis. The Heyes and Melrose potential free algorithm for hard sphere interactions is an alternative modeling technique [41], which will be employed here. The algorithm allows particles to overlap during integration of the equations of motion, then searches for overlapping pairs and increases their interparticle separation until they just contact. This process may be repeated iteratively to resolve multiple particle overlaps to within a prescribed tolerance.

For over-damped particle dynamics, the Heyes and Melrose iterative process can be functionally modeled with an interaction potential that resembles a Hookean spring. In the absence of hydrodynamic interactions, the harmonic potential has to have the form

\[ U_{HS}(r) = \frac{3\pi \eta_s a}{2\Delta t} (2a - r)^2 \mathcal{H}(2a - r), \tag{2.15} \]

where the Heaviside step function \( \mathcal{H}(r) \) ensures that potential acts only on overlapping particles. However, if the particle pair interacts hydrodynamically via the RPY tensor, the correct form of the interparticle potential that returns them to contact is:

\[ U_{HS}(r) = \frac{16\pi \eta_s a^2}{\Delta t} \left( 2a \log \left( \frac{2a}{r} \right) + r - 2a \right) \mathcal{H}(2a - r), \tag{2.16} \]

Using forward Euler integration of the over-damped equations of motion, one can show that the relative displacement as a result of the potentials in (2.15) and (2.16) is exactly sufficient to put the hydrodynamically noninteracting and interacting colloids, respectively, back into contact.

This model works very well for the inelastic collisions of overdamped colloids as it converges to the hard sphere potential as \( \Delta t \to 0 \). Additionally, this approach is guaranteed to not diverge and has the advantage of being athermal, which means the relevant hard sphere potential is independent of any other energy scale in the system [42]. It can be adapted without alteration to simulations of flowing processes and it can be combined with any other potential.
Short-ranged attraction

Attraction between like colloids can be facilitated by a number of physical forces including van der Waals forces, dipole-dipole interactions, forces due to polymer bridging, hydrophobic forces, and forces due to dissolved polymer. This last class of attractive interactions, sometimes termed depletion attraction, is of interest because it is easily realized and controlled experimentally. The addition of non-adsorbing polymer to a colloidal dispersion can produce fine scale differences in osmotic pressure. When the polymer is excluded from the region between nearly touching particles, the osmotic pressure difference on the opposite sides of the colloids leads to a net force that pushes the particles together. The particles effectively feel an attraction due to the presence of the polymer, the strength of which is equal to the product of the ideal solution osmotic pressure of the polymers and the volume of the gap that these cannot penetrate [7]. The Asakura-Oosawa potential [43] describing this depletion attraction is applied in the model systems throughout this work. It is given by:

\[
U_{AO}(r) = \begin{cases} 
0, & r < 2a \\
-U_A \frac{2(2(a+R_g))^2-3r(2(a+R_g))^2+r^3}{2(2(a+R_g))^2-6a(2(a+R_g))^2+2a^3}, & 2a \leq r < 2(a + R_g) \\
0, & r \geq 2(a + R_g) 
\end{cases}
\] (2.17)

In experiments, the strength and range of the potential can be controlled by the polymer concentration and size respectively. In simulations the potential is modulated through the strength at contact, \(U_A = U_{AO}(2a)\), linearly proportional to the polymer concentration, and the ratio of polymer to colloid size, \(\delta = R_g/a\). For all model systems considered, \(\delta \leq 0.15\), so that the potential is indeed short-ranged and the assumption of pair-wise additivity of attractive potentials is well founded [7]. Ultimately, the interaction potential of attractive colloids in the model systems is the sum of the hard sphere and the Asakura-Oosawa potential, \(U(r) = U_{HS}(r) + U_{AO}(r)\) and the interparticle force is given by \(F^p(r) = -\nabla U(r)\). Equation (2.17) is strictly only valid for equal sized particles, since the volume of the polymer depleted region between attractive colloids will depend on their relative radii. In instances, when polydisperse systems are modeled, the appropriately modified version of (2.17) is employed [7].
The equilibrium phase diagram of the short-ranged depletion attraction is well described by thermodynamic theory [7]. As confirmed by experiments, there is a wide region of coexistence between a dilute liquid and a solid crystalline phase [10]. However, for a large number of conditions, the process of phase separation is often interrupted or masked by a percolation transition [9], illustrated in figure 2-1. The percolation line demarcates transient cluster and network forming regions, in which colloidal gels form as a result of kinetic arrest, the focus of this thesis.

![Phase Diagram](image)

Figure 2-1: Schematic picture of the phase diagram of a short-range attractive colloidal dispersion. Within the colloidal fluid-solid coexistence (black curve) the phase separation can go to completion (hatched region) or the metastable liquid can undergo percolation (purple line) masking the fluid-fluid spinodal decomposition (red curve). The shaded region of the phase diagram represents colloidal dispersions where a single fluid phase is thermodynamically stable.

**Long-ranged repulsion**

In an ionic solvent, colloids often acquire a surface charge that can lead to long-ranged repulsive interactions between particles. Counterions in the suspending solvent gather near the particles forming electrostatic double layers, effectively screening the repulsive interactions [8]. A simple potential often used to describe screened electrostatic interactions is the
Yukawa potential, given by

\[
U_R(r) = \begin{cases} 
0, & r < 2a \\
\frac{Aa}{r} \exp(-\kappa_D r), & 2a \leq r \geq r_{cut} \\
0, & r > r_{cut},
\end{cases}
\]  

(2.18)

where \( A \) measures the strength of the potential and the Debye length \( \kappa_D^{-1} \) reflects the effective range of the Coulombic repulsion. The Debye length is modulated through the addition of salt and the strength of the potential is determined by the chemistry of the system and the size of the particles \[44\]. A cutoff distance of \( r_{cut} \kappa_D = 10 \) is introduced for computational convenience, as the interaction strength is effectively zero for such large separations.

The combined potential of a colloidal dispersion with short-ranged attraction and long-ranged dispersion is modeled using the potential \( U(r) = U_{HS}(r) + U_{AO}(r) + U_R(r) \) and \( \mathbf{F} = -\nabla U(r) \), as before. For particles separated by a dimensionless gap greater than \( \delta \), the repulsive part of the potential will serve to keep the colloids well dispersed.

### 2.3 Simulation method

The evolution of particle trajectories and consequently the outcome of discrete element simulations using the overdamped Langevin equation is strongly influenced by the representation chosen for the hydrodynamic mobility, \( \mathbf{M} \).

As discussed in section 2.1.1, \( \mathbf{M} \) is a dense matrix, which couples all the forces on the particles to their velocities and can only be found at great computational expense through solution of the Stokes equations in the fluid phase surrounding the particles. The exact form is known only for a few particle configurations such as isolated pairs of spherical particles. For any other configuration it can be approximated with varying degrees of accuracy.

When neglecting hydrodynamic interactions, \( \mathbf{M} \) is a diagonal matrix with a single eigenvalue: \( 1/6\pi \eta_s a \), which is the Stokes mobility \[45\] and depends only on the solvent viscosity and the hydrodynamic radius of the particles. This gives the particles the Stokes-Einstein diffusivity: \( D = kT/6\pi \eta_s a \) and defines the bare diffusion time scale, \( \tau_D \), as before. Simu-
lation methods, which use the configuration independent mobility tensor as a crude model for the exact $M$—known as the freely draining approximation (FD) [46]—are traditionally simply referred to as Brownian Dynamics (BD).

According to (2.9), when $M = I/(6\pi \eta a)$, the particle positions evolve in response to a force that is the gradient of the potential energy landscape. This fact sets the BD method apart from all other approximations of $M$ employed in simulations. The particles effectively move along fastest descending paths to the local energy minima, facilitating the evolution of the system to thermodynamic equilibrium. In contrast, for any other, more complex approximation of the mobility tensor, the motion of the particles is strongly coupled and hence the particles will evolve along alternative kinetic pathways to different local states without a guarantee to attain a global minimum. For simulations of kinetically arrested materials this evidently bears significant consequences and is the motivating reason for several investigations in chapters 3 and 4 of this thesis.

Out of the many hydrodynamic models published in the literature, the Stokesian Dynamics (SD) paradigm represents hydrodynamic interactions between Brownian colloidal particles with particularly high fidelity. The higher accuracy representation of the fluid mechanics follows directly from systematically extending the multipole expansion to higher order (e.g. torque and stresslet). Three-body and higher-order multi-body effects could be incorporated to arbitrary order, but since the hydrodynamic scattering series only converges slowly it is closed by separating the hydrodynamic force into near-field (or lubrication) and far-field contributions and introducing the exact two-body lubrication contribution to the hydrodynamic resistance. This leads to a force balance constraint and necessitates computationally costly matrix inversions to advance the particle trajectories [47]. Accelerated Stokesian Dynamics [39,48] is an efficient implementation of this paradigm for discrete element simulations, which has recently been accelerated further by incorporating the spectral Ewald method [49].

One simpler approximation with high computational efficiency is the Rotne-Prager-Yamakawa tensor, which accounts pair-wise only for the long-ranged hydrodynamic interactions between particles of hydrodynamic radius $a$. It couples the non-hydrodynamic forces exerted on particle $\beta$ to the motion of particle $\alpha$ with a center-to-center unit vector $\hat{r}$. The
The explicit form of the RPY tensor \[50,51\] is given by:

\[
M_{\alpha\beta} = \begin{cases} 
\frac{1}{6\pi\eta_a} I & \text{if } \alpha = \beta, \\
\left(1 + \frac{a^2}{3} \nabla^2\right) \frac{1}{8\pi\eta_r} (I + \hat{f}\hat{f}) & \text{if } \alpha \neq \beta \text{ and } r \geq 2a, \\
\frac{1}{6\pi\eta_a} \left[(1 - \frac{9r}{32a})I + \frac{3r}{32a}\hat{f}\hat{f}\right] & \text{if } \alpha \neq \beta \text{ and } r < 2a,
\end{cases}
\tag{2.19}
\]

The RPY tensor can be thought of as the leading order perturbation to the Stokes mobility in a Taylor series expansion of \(M\) about large interparticle separations. Even though the use of the RPY tensor in place of \(M\) does not fully account for many-body hydrodynamic interactions, it represents the first order improvement over Brownian dynamics and it allows introduction of far-field hydrodynamics into the numerical simulation in a controlled manner. The significant element of the RPY model is that it accurately reproduces the long-ranged hydrodynamic interactions between colloids. It thus incorporates the collective motion of particles abundant in diffusing, aggregating and sedimenting dispersions of colloidal aggregates \[52,53\] and is indispensable for the quantitative evaluation of transport properties. For translationally invariant systems, considered in this work, the divergence of the RPY mobility appearing in the final stochastic drift term in (2.9) vanishes, so that particle trajectories evolve along:

\[
x(t + \Delta t) = x(t) - M \cdot F^\alpha \Delta t + \Delta x^R(t) 
\tag{2.20}
\]

The RPY hydrodynamic model has several computational advantages over Stokesian Dynamics and other methods. As lubrication forces and high-order contributions to the hydrodynamic scattering series are neglected, the matrix inversion in simulations can be avoided, which results in a significant reduction of numerical complexity. This enables rapid simulations of much larger gelling systems at the expense of model fidelity. Subsequent chapters, where relevant, will discuss the consequences of this tradeoff and introduce added layers of complexity when necessary.
2.3.1 Implementation

Almost all previous computational work in the field has performed simulations of Brownian particles on central processing units (CPU). However, due to their high parallelizeability, graphics processing units (GPU), originally created to render graphics, surpass the computational power of CPUs in terms of floating point operations per second. Only recently though have GPUs been flexible enough to provide a general programming platform. One molecular dynamics (MD) program optimized for massively parallel processing on GPUs is the HOOMD-blue suite of MD simulation software [54–56] for NVIDIA GPUs.

For the investigations in this thesis, Brownian Dynamics simulations were run natively in HOOMD-blue, while the RPY simulations utilized a custom plug-in to HOOMD-blue built for performing large scale hydrodynamic calculations on the GPU [57]. This plug-in executes a version of the particle-mesh-Ewald method for the modeling of Stokes flows in periodic domains [58] and Fixman’s Chebyshev polynomial approximation is used to compute the Brownian displacement at each time step in these simulations [59]. Using this approach utilizing HOOMD-blue on a single GPU enables faster than real-time simulation of non-trivial suspension volumes with up to $O(10^4)$ particles. This speed at large scale is essential to modeling the kinetic processes of interest accurately and enabled many of the results presented in chapters 3 and 4.

However, the studies of flow phenomena described in chapters 7 –9 required computer simulations of order of magnitude larger system sizes that would have been unfeasible to perform effectively using the above described custom plug-in. Recent advances in the research group have led to the development of a novel method for the rapid calculation of hydrodynamic interactions in suspensions of spheres [37]. The positively-split Ewald (PSE) algorithm makes the cost of computing Brownian displacements in simulations of colloidal scale particles with hydrodynamic interactions comparable to the cost of computing deterministic displacements in conventional BD simulations. The method relies on a new, but mathematically equivalent positively-split formulation to (2.19) for the Ewald summation of the RPY tensor, which guarantees that the real-space and wave-space contributions to the tensor are independently symmetric and positive-definite for all possible particle config-
urations. The normally costly Brownian displacements are drawn from a superposition of two independent samples: a wave-space (far-field) contribution, computed using techniques from fluctuating hydrodynamics and non-uniform fast Fourier transforms; and a real-space contribution, computed using a Krylov subspace method. The combined computational complexity of drawing these two independent samples scales linearly with the number of particles enabling hydrodynamic simulations with system sizes up to $4 \times 10^6$ particles and is currently the fastest algorithm for simulations of Brownian particles employing the RPY tensor. This has made it possible to perform dynamic simulations of colloidal gels over unprecedented length and time scales leading to many important observations and novel results presented in this thesis.

As described earlier, in the RPY method hydrodynamic interactions for spherical particles are summed pair-wise, but three-body and higher-order multi-body effects are neglected to first order. A next order correction would consider the rigid body motion of the immersed colloids. Rigid particles cannot deform with the local fluid strain, and as a result they acquire a symmetric force dipole that produces additional disturbance flows to resist this deformation. As this increases the viscous dissipation in the fluid it could be argued that it might qualitatively affect the behavior of colloidal gels and a correct representation of rigid body motion is therefore required to compute accurate transport properties. This question is addressed systematically in both chapters 6 and 7 using the Force-Torque-Stresslet (FTS) simulation method. FTS is an extension of the PSE algorithm to the same level of hydrodynamic approximation by accounting for the additional multipole moments corresponding to the hydrodynamic torque and stresslet through computation of the nine elements of $\mathcal{M}$, as introduced in (2.3). It leverages the same positively-split formulation for the RPY tensor and a mid-point integration scheme to efficiently solve the resulting stochastic differential algebraic equations for $\mathcal{O}(10^6)$ particles [60].

By default, the simulation box is cubic, unless noted otherwise. Three-dimensional periodic boundaries are employed to represent an unbounded system. In the overdamped limit in HOOMD-blue all quantities are made dimensionless on the characteristic particle length scale, $a$, the thermal energy scale, $kT$ and the diffusive time scale, $\tau_D$, while all other quantities can be derived from these three. The duration of the simulations is measured in terms
of the number of diffusive steps modeled with a time step: $\Delta t = 10^{-4} \tau_D$. This ensures that the dynamics of the dispersion are well resolved.

### 2.4 Model system

Throughout this thesis certain commonalities are employed for all models of colloidal dispersions. The colloids are suspended in an incompressible Newtonian fluid with viscosity $\eta_s$ and are modeled as rigid, no-slip spherical particles with identical hard sphere and hydrodynamic radius $a$ and zero poly-dispersity, $d_a = 0$, unless noted otherwise. The number of colloids modeled in each simulation is $N$, which together with the volume fraction of particles, $\phi = \frac{4\pi}{3} a^3 N / L^3$, defines the characteristic size, $L$, of the simulation box considered.

An attractive colloidal dispersion in the absence of external forcing is fully described by three system parameters. These are $\phi$ and two dimensionless quantities characterizing the attraction. The characteristic energy scale is the ratio of the strength of the interparticle bond at contact, $U_A$, relative to $kT$. When necessary, the parameter $\epsilon = kT/U_A$ will be used to vary the interparticle attraction from the athermal limit, $\epsilon = 0$, to the hard sphere limit, $\epsilon \to \infty$. $\delta = \Delta/a$ measures the range of the attractive potential relative to the particle size.

As mentioned above, in the specific case of the depletion potential $\Delta = R_g$.

When necessary, shear flow with an adjustable strain rate $\dot{\gamma}$ is implemented using Lees-Edwards boundary conditions [61]. These generate a superimposable shear flow velocity profile where the local average velocity relative to the center of the periodic domain is directly proportional to the vertical position. The two relevant system parameters here are the Mason number, $Mn = 6\pi \eta_s a^2 \Delta \dot{\gamma} / U_A$, measuring the shear force exerted on a particle relative to the bond force of the particle pair at contact, and the Péclet number, $Pe = 6\pi \eta_s a^3 \dot{\gamma} / kT = Mn / (\delta \epsilon)$, representing the relative rate of shearing to the bare diffusive time scale. To study a colloidal gel in a gravitational field, the deterministic nonhydrodynamic force employed in the simulation is appended with an external gravitational body force, i.e. $F^P = -\nabla U + F^G$. The gravitational Mason number, $G = |F^G| a / U_A$, quantifies the gravitational load relative to the interparticle bond strength.
Chapter 3

The Role of Hydrodynamic Interactions in Colloidal Gelation

3.1 Introduction

Although equilibrium thermodynamics dictates the stability of different phases within a dispersion of attractive colloids, the mechanism of phase separation is controlled by physical transport processes. Macroscopic phase separation typically takes on one of two forms: nucleation and growth, or spinodal decomposition [62,63]. The boundary between these growth regimes depends on how fluctuations arise and are dissipated within the phase separating material. In particular, past work on binary liquid-liquid phase separation has shown that structure and kinetics are sensitive to hydrodynamic flows in the phase separating material [64,65].

A long standing question regarding colloidal gels is the role of these hydrodynamic forces in determining the gel microstructure and gelation kinetics [29]. Figure 3-1 shows the terminal state of discrete element simulations using two different models for interparticle hydrodynamic interactions under identical thermodynamic conditions. The gelation kinetics and gel microstructure depend on the dissipation mechanisms within the gel. Consequently, the rheology, coarsening and stability of colloidal gels at different ages should exhibit a sensitivity to hydrodynamic interactions between particles. As described in chapter 2, these interactions are fundamentally long-ranged, which makes their mathematical description in
theoretical and computational models problematic [30, 31]. The construction of parsimonious discrete element models for colloidal gelation is important in order to understand how micro-mechanics within the arrested material give rise to macroscopic material properties that are ultimately needed for engineering applications.

In the past, a number of discrete element simulations have been employed to model the microstructural evolution of gels. The results of the simplest simulation method, Brownian Dynamics (BD) are gels which form at higher concentrations and attraction strengths than observed in experiments. Typically, the distributions of nearest neighbors for particles in the gel is higher than expected from experiment [66]. An alternative model, Fast Lubrication Dynamics (FLD), was used by Bybee and Higdon [67] and incorporates only lubrication interactions between nearly touching particles as a model of the interparticle hydrodynamics. They found that there was no detectable shift in the percolation line or microstructure of the gel with respect to BD and concluded that lubrication introduces only a weak shift in the gelation time scale.

Furukawa and Tanaka [68] modeled gelling colloids as viscous drops and incorporated the hydrodynamic interactions between particles via their Fluid Particle Dynamics (FPD) method. Gelation in their simulations was diffusion limited, and they observed a shift in the percolation line with respect to BD simulations. This shift was consistent with experimental observations; however, no mechanism was demonstrated that could explain the shift. Cao, Cummins and Morris [69] employed Stokesian Dynamics (SD) as a model for interparticle hydrodynamic interactions in gels formed via reaction limited aggregation. They found a shift in the percolation line similar to Furukawa and Tanaka, and attributed the shift to the dynamics of restructuring within small aggregate clusters. How this slowing in the internal dynamics of small clusters leads to broad shifts in the percolation line was not explored.

Such detailed simulation methodologies (FLD, FPD, SD) come at great expense. All these models except BD, employ 1500 particles or fewer, so that the system size is in all cases on the same order of magnitude or smaller than the pore size in the gels that form. Whether this small system size stabilizes or destabilizes nascent gels is a separate, open question. For certain, however, models which are capable of simulating larger system sizes over feasible time scales should be preferred. In the periodic geometries necessitated by computational
simulation of infinite systems, the lattice dimension can have a significant impact on the hydrodynamic flows that particles generate [48]. In order to screen out system size effects in hydrodynamic interactions between particles, large system sizes are desirable when modeling kinetic phenomena such as gelation.

![Figure 3-1: Attractive particle dispersions with $\phi = 10\%, U_A = 5kT$, and $\delta = 0.1$ after 300 bare diffusion times. Left: without hydrodynamic interactions, right: with long-ranged hydrodynamic interactions. The right sample is gelled while the left is a dispersion of condensed droplets. Color is used to call out monomers, dimers, trimers, each other n-mer, and the system spanning cluster.](image)

Four competing hydrodynamic models (BD, FLD, FPD, SD) have shown that the percolation line in colloidal gelation is sensitive to hydrodynamic interactions. The mechanism for this sensitivity is still unclear, however. BD, which neglects hydrodynamic interactions, and FLD, which includes only the short-ranged, divergent dissipative forces between particles, show higher mean contact number and percolation at higher strengths of attraction than SD and FPD simulations of similar processes. SD and FPD model both the short-ranged lubrication forces and long-ranged hydrodynamic interactions with reasonable fidelity. By elimination, long-ranged hydrodynamic interactions seem a likely candidate for the microstructural differences between models. We hypothesize that these long-ranged hydrodynamic interactions are key for colloidal gelation.

In this chapter we test this hypothesis by employing the Rotne-Prager-Yamakawa tensor (RPY) [50,51] that accounts for only long-ranged interactions between particles. Section 3.2 describes the RPY and BD simulations of gelation, where the same disparity in percolation
and mean contact number is observed as with SD and FPD simulations of gelation. The results presented in 3.3 confirm that long-ranged hydrodynamic interactions are sufficient for establishing the gel boundary, structure and coarsening kinetics observed in experiments and more sophisticated simulation methods. Section 3.4 presents a simple macroscopic model of coagulation and compaction of particulate aggregates that is used to explain why BD and FLD simulations fail to produce gels consistent with experimental evidence while SD, FPD and RPY simulations reflect experimentally observed structure and kinetics with much greater fidelity.

3.2 Simulation details

The exact hydrodynamic mobility $M$ is a dense matrix which couples all the forces on the particles to their velocities and is known only for a few particle configurations such as isolated pairs of spherical particles. For any other configuration, it can be approximated with varying degrees of accuracy using SD, FLD, FPD. One approximation with high computational efficiency is the RPY tensor, which accounts only for the long-ranged hydrodynamic interactions. As discussed in chapter 2, even though the use of the RPY tensor in place of $M$ does not fully account for many-body hydrodynamic interactions, it represents the first order improvement over BD and it allows introduction of far-field hydrodynamics into the numerical simulation in a controlled manner. While without lubrication forces the motion of particles during small n-mer aggregations will not be represented correctly, RPY simulations will accurately capture the hydrodynamics interactions between and relative mobility of large aggregates, where there are no lubrication forces between particles present [31]. We expect this to be crucial for subsequent network formation and gelation [70].

Additionally, the reduced complexity of the RPY tensor enables rapid simulations of several orders of magnitude larger gelling systems than SD or FPD at the expense of model fidelity. Figure 3-2 plots the streamlines of the flow field generated by a point force in periodic Stokes flow. This is the principal, long-ranged flow generated by particulate motion, and as indicated in the figure, the streamlines are scale independent. In order to screen out system size effects in hydrodynamic interactions, models which are capable of simulating
Figure 3-2: The Stokes flow streamlines produced by a horizontally moving particle (solid) in a periodic domain. The particles occupies 8 times more volume in the plot on the right. The translucent particles are positioned at equivalent interparticle separations relative to their radii, but are entrained differently by the periodic Stokes flow. The size of the periodic domain can have a significant impact on how other particles interact hydrodynamically.

larger system sizes over feasible time scales should be preferred.

Particle dispersions with radius $a$ and an attractive depletion attraction [43] were simulated with and without hydrodynamic interactions at 5 volume fractions: $\phi = 5\%, 10\%, 15\%, 20\%, 25\%$. The strength of the interparticle attraction, $U_A$, was varied relative to the thermal energy $kT$, and the range of the interparticle attraction was restricted to interparticle separations smaller than $2a(1 + \delta)$, with $\delta = 0.1$. Simulations were run for an initial 100 single particle diffusion steps, $\tau_D = 6\pi \eta_s a / kT$, without interparticle attractions to ensure thermal equilibration, and for subsequent $300\tau_D$ with the attraction turned on.

The number of particles used in the simulations was $N = 8,000$ with hydrodynamic interactions and $N = 64,000$ without. Simulations were run with $N = 2,000$ and $N = 6,000$ for each of these two cases as well. In subsequent figures, only data for the largest simulations is reported for clarity. We show the structure factors for identical conditions but at different system sizes obtained with both RPY and BD in figure 3-3. The static structure factor,

$$S(q) = \left\langle \frac{1}{N} \sum_{j,k=1}^{N} \exp \left( i \mathbf{q} \cdot (\mathbf{x}_j - \mathbf{x}_k) \right) \right\rangle,$$

which quantifies spatial correlations between particle positions over distances $\approx 2\pi/q$, is
Figure 3-3: Static structure factor at $U_A = 6kT$, $\delta = 0.1$, $\phi = 10\%$ and $t = 300\tau_D$ for BD and RPY simulations at three different system sizes: $N = 2,000, 6,000, 8,000$ and $64,000$ (BD only). For clarity, a constant vertical offset of 5 units was added between structure factors (except for BD $N = 2,000$). Sample to sample fluctuations over ten (BD) or five (RPY) independently generated instances correspond to deviations of $\pm 3\%$ - error bars not shown.

especially independent of $N$, with the peak at $q \approx 4$ indicating the contribution of bonded particles. At the analyzed conditions the system is found to be dynamically percolated, and as such the peak in $S(q)$ at small wave vectors ($q \to 0$) is indicative of system spanning network formation and suggests that no systematic system size effects are present.

However, at the smallest values of $q$, differences in the structure factor as a function of system size emerge, since naturally the spatial correlations on the length scale of the simulation box are dependent on the box size and hence the number of particles $N$ at fixed $\phi$. While there is no guarantee that the sizes studied are sufficient to establish system size independence, the system sizes studied here represent the largest simulated systems accounting for far-field hydrodynamics reported to date.
3.3 Results

Under many equivalent conditions, the RPY simulation results in a gelled dispersion that has pore sizes significantly smaller than the periodic simulation domain, while the BD simulation results in a phase of dispersed, highly crystalline domains (see figure 3-1). Characterization of the gel state proceeds by identifying all bonded particles pairs that are within the range of the attractive well and constructing an adjacency matrix that is searched for clusters. The largest cluster is system spanning and dynamically percolated if on including the simulation’s periodic images, the new adjacency matrix contains a path connecting the cluster to its periodic images in all three dimensions (see appendix A). Above the percolation threshold, almost all particles (more than 99%) belong to a persistent, connected network of particles spanning the whole system.

3.3.1 The depletion phase diagram

A phase diagram for the dispersions determined from BD and RPY simulations is depicted in figure 3-4. The dashed black line corresponds to the fluid-crystal binodal given by scaled particle theory [7]. The RPY simulations exhibit gelation at lower strengths of attraction than those where hydrodynamic interactions were neglected. The lower threshold resides entirely within the fluid-crystal binodal. The minimal percolation point to within 0.1kT was determined in each case over three independently generated samples for both the BD and RPY models and is indicated on the phase diagram by the solid and dashed blue curves, respectively. The gap between the percolation thresholds is roughly 1kT at all but the lowest volume fraction studied. At \( \phi = 5\% \) no percolation is observed for BD simulations, while for RPY simulations gelation occurs for attractions \( U_A \geq 6kT \). As simulations at such low volume fractions are quite slow, the precise location of the RPY percolation boundary is difficult to identify. For Brownian Dynamics simulations that failed to gel, simulations were run an additional \( 10^4 \) bare diffusion times to confirm that no percolation occurs.

These simulations are particularly interesting because the conditions correspond almost exactly to the seminal experimental work with depletion gels by Poon and coworkers [71]. In their work, depletion attraction strengths near \( 4.0kT \) produced gels from dispersions with...
Figure 3-4: Top: Phase diagram for attractive particle dispersions with $\delta = 0.1$. Nonequilibrium phases are indicated with filled symbols for simulations in the absence of hydrodynamic interactions and open symbols with hydrodynamic interactions. Bottom: Comparison of simulations with experiments from Poon and coworkers [71]. The interaction potentials are normalized by the co-existence values ($U_{coex}$) at each volume fraction $\phi$. The difference between the experiments and the simulations is the polymer size ratio which was estimated to be 20% smaller in the experiment, $\delta = 0.08$. The blue dashed and solid lines indicate the percolation boundary in RPY and BD simulations respectively.
particle volume fractions between 5% and 20%. The ratio of polymer radius of gyration to particle radius was estimated to be 0.08, and the particles were prepared such that in the absence of polymer they exhibited purely hard sphere characteristics. Their observation of the formation of a percolated network is consistent with the RPY simulations. BD simulations fail to replicate this observed nonequilibrium phase behavior. Accounting for long-ranged hydrodynamic interactions through the RPY tensor yields an improved agreement with experiments. In BD far higher attraction strengths and volume fractions are needed to produce a gel when compared with experiments, and a broad set of attraction strengths yield complete phase separation into small crystal nuclei instead of gelation.

Figure 3-5: Contact number distributions for attractive particle dispersions after 300 bare diffusion times with \( \phi = 10\%\), 15\% and 20\%, \( \delta = 0.1\), \( U_A = 5kT\) (left) and \( U_A = 7kT\) (right).

This observation is corroborated by the contact number distributions shown in figure 3-5. For dispersions with 10\%, 15\% and 20\% particles by volume and \( U_A = 5kT\) and \( 7kT\), the terminal contact number distribution in BD and RPY simulations was determined. This measure gives the probability of finding a particle having a number of neighbors with an interparticle separation smaller than \( 2a(1 + \delta)\). For the weaker attraction, the contact number
distribution from BD simulations displays a high degree of crystallinity in contrast to the RPY simulations where gelation is observed at all volume fractions. For the stronger attraction, the models show similar contact number distributions with peaks near the Maxwell isostaticity condition, \( N_c = 6 \) [72]. Notably, the BD simulations exhibit many more particles with contact numbers greater than six.

### 3.3.2 Dynamic relaxation during gelation

An outstanding question is the effect of hydrodynamic interactions on collective dynamical processes as the gel forms, studied here, and in gels at rest, explored in chapter 6. The strong dependence of microscopic dynamics on the probed length scale close to gelation has been studied experimentally [73] as well as numerically [21, 74] - however, without considering hydrodynamic interactions. The incoherent scattering function,

\[
F_S(q, t) = \left\langle \frac{1}{N} \sum_{j=1}^{N} \exp \left( -i \mathbf{q} \cdot (\mathbf{x}_j(t) - \mathbf{x}_j(0)) \right) \right\rangle,
\]

quantifies the time correlation in single particle displacements over a length scale \( \approx 2\pi/q \) and a time lag \( t \), whereas the coherent scattering function,

\[
F(q, t) = \left\langle \frac{1}{NS(q)} \sum_{j,k=1}^{N} \exp \left( -i \mathbf{q} \cdot (\mathbf{x}_k(t) - \mathbf{x}_j(0)) \right) \right\rangle,
\]

provides information on the collective dynamics of the system.

The decay of the correlations from their initial plateau is indicative of network restructuring and relaxation and can be fitted by a stretched exponential \( \sim \exp[-(t/\tau_q)^\beta] \), where \( \tau_q \) is the structural relaxation time and \( \beta \) is a stretching exponent. \( \beta \) is strongly dependent on the shape of the distribution of relaxation modes, wider distributions leading to lower exponents.

\( F_S(q, t) \) and \( F(q, t) \) as a function of the normalized lag time \( t/\tau_q \) for a set of wave vectors, are shown in figures 3-6 and 3-7 for two gels under different conditions obtained in BD and RPY simulations. For both simulation methods the relaxation times are found to scale as
Figure 3-6: The incoherent scattering function $F_s(q, t)$ for BD and RPY gels of $\phi = 15\%$, $\delta = 0.1$, $U_A = 5kT$ and $7kT$ for selected wave vectors $q$ at $t = 10^2 \tau_D$. For clarity, a constant vertical offset of 0.5 units was added between sets of $F_s(q, t)$. The dashed lines present the trivial exponential $\exp[-t/\tau_q]$, highlighting the compressed and stretched nature of the scattering function decay. Sample to sample fluctuations over four independently generated instances correspond to deviations of $\pm 3\%$ - error bars not shown. Inset: the characteristic relaxation time $\tau_q$ as a function of $q$ for the four different gels - colors are the same as in the main plot.

$\sim q^{-2}$ – the single-particle as well the collective modes exhibit diffusive dynamics. Instead of a two-step decay as reported elsewhere [21,74], we do not observe an inertial decay at any wave-vector, presumably since our simulations are truly overdamped and inertial relaxation (the fast relaxation process) is instantaneous.

Comparing RPY and BD simulation results, it is apparent that long-range hydrodynamic interactions change gelation dynamics and generate different transport processes in the network for weak gels ($U_A = 5kT$) just above the gelation boundary. Ultimately, these differences arise from the depth of the quench into the phase separating region and indicates that the gelation boundaries are truly different in BD and RPY, with the hydrodynamic
Figure 3-7: The coherent scattering function $F(q,t)$ for BD and RPY gels of $\phi = 15\%$, $\delta = 0.1$, $U_A = 5kT$ and $-7kT$ for selected wave vectors $q$ at $t = 10^2\tau_D$. For clarity, a constant vertical offset of 0.5 units was added between sets of $F(q,t)$. The dashed lines present the trivial exponential $\exp\left[-t/\tau_q\right]$, highlighting the compressed and stretched nature of the scattering function decay. Sample to sample fluctuations over four independently generated instances correspond to deviations of $\pm 2\%$ - error bars not shown. Inset: the characteristic relaxation time $\tau_q$ as a function of $q$ for the four different gels - colors are the same as in the main plot.

Simulations agreeing with experiments. In BD, decay of $F_s(q,t)$ is rapid, with a stretched exponent over all length scales of $\beta \approx 0.4$, signifying that the structure has not come to full arrest and the relaxation dynamic are complex and slow. Since we observe a high amount of crystallinity at these conditions (see figure 3-5), such low stretching exponents may be due to both $\alpha-$ and $\beta-$relaxation occurring in the dispersion [75]. Consequently, the collective modes exhibit a narrow relaxation spectrum with little long-range correlation.

At the same conditions for RPY, when long-ranged hydrodynamics are considered, the gel is fully arrested and dynamics are dependent on the size of the region under analysis. For small $q$, $F_s(q,t)$ decays close to exponentially ($\beta \approx 1$). However, for smaller length
scales, the decay of the correlations is stretched, with \( \beta \) decreasing linearly and approaching a value close to \( \sim 0.5 \), suggestive of a broad relaxation spectrum. The decay of \( F(q, t) \) is also broadened compared to BD, hinting that dynamics are affected by the restructuring of the network and that the dispersion is characterized by strong cooperativity due to the presence of long-range hydrodynamic interactions. In contrast, as already observed in the case of the terminal contact number distribution, strong gels far from the boundary \( (U_A = 7kT) \) are less sensitive and exhibit similar dynamics. However, observable differences in the relaxation mechanisms persist both for the single-particle and collective motion.

Measurements of the particle dynamics in the percolated system shows that the long-range correlations and particle cooperativity near the gelation boundary are sensitive to hydrodynamic interactions between colloids and hence aggregate diffusion rates. Changes in the organization and in the kinetics of restructuring of the network due to hydrodynamic interactions ultimately determine the terminal state of an attractive dispersion and hence influence the location of the observed dynamic percolation line.

3.4 The effect of hydrodynamic Interactions on aggregation kinetics

Gelation occurs when the dispersed phase of a suspension becomes meta-stable or unstable with respect to a condensed phase. The kinetics of the transition to the condensed state on quenching from the dispersed one are controlled by two competing processes: compaction of individual aggregates, which seeks to maximize interparticle contacts and minimize surface energy, and coagulation of different aggregates. This is true whether the mechanism for gelation is spinodal or nucleation driven. When compaction is much faster than coagulation, the condensed phase of the suspension will tend to have minimal volume and surface area, and phase separation will proceed to completion. When compaction is much slower than coagulation, the condensed phase will be space spanning and have high surface area. If the resulting gel coarsens slowly enough, phase separation appears to arrest. The onset of gelation is observed when these two rate processes are comparable.
The rate of compaction is set by the Kramers hopping of particles within an aggregate between different meta-stable configurations [76]. Theories for chemical kinetics evaluate transition rates from one meta-stable state to another from a properly weighted sampling of different paths through such a landscape. However, Kramers theory for such rate processes indicates that the kinetics are dominated by the magnitude of energy barriers at suitable transition states in the landscape: $\Delta U$. The time scale associated with the compaction process is proportional to $e^{\Delta U/kT}$, and the coefficient of proportionality has only a mild sensitivity to the energy dissipation mechanism: hydrodynamic interactions between the particles [38]. The height of the energy barriers resisting compaction are difficult to estimate since these barriers are highly configuration dependent. In general these should be proportional to the strength of attraction $U_A$, and the time scale for compaction should increase exponentially as attractions between particles grow stronger due to growth of these energy barriers.

There is an additional rate process to consider: the break-up of aggregates. Like the time scale for compaction, this is also set by a Kramers escape time, $\tau_K$. For a particle bound by depletion interactions this time scale is: $\tau_K/\tau_D = \delta^2 e^{N_b U_A/kT}$ where $N_b$ is the number of bonds between particles that would need to be broken for the particle to escape. This ratio is more than four for $N_b \geq 2$ and $U_A/kT \geq 3$ and grows exponentially with respect to both. Therefore, in the domain of interest, break-up of all but the smallest aggregates occurs at a vanishingly small rate.

The mean-field Smoluchowski coagulation equation governing the time rate of change of the number density of aggregates containing $i$ particles, $n_i(t)$, depends on the coagulation rate of other diffusing aggregates [77]:

$$\frac{\partial n_i(t)}{\partial t} = \frac{1}{2} \sum_{j=1}^{i-1} K(i-j,j)n_{i-j}(t)n_j(t) - \sum_{j=1}^{\infty} K(i,j)n_i(t)n_j(t).$$

(3.4)

$K(i,j)$ is the so-called coagulation kernel that describes the rate at which aggregates containing $i$ and $j$ particles collide and cohere within the dispersion, and can be written as:

$$K(i,j) = 4\pi(a_i + a_j)D_{ij}/W_{ij}.$$  

(3.5)
where, $a_i$ is the collision radius of an aggregate with $i$ particles, $D_{ij}$ is the relative rate of bare diffusion between aggregates of size $i$ and $j$, and $W_{ij}$ is the collision efficiency:

$$W_{ij} = (a_i + a_j) \int_{a_i + a_j}^{\infty} \frac{D_{ij} e^{U(r)/kT}}{r^2 D_{ij}(r)} dr.$$  \hspace{1cm} (3.6)

$D_{ij}(r)$ reflects the reduction in relative diffusivity due to hydrodynamic interactions between two aggregates. As $r \to \infty$, $D_{ij}(r) \to D_{ij}$. The coagulation kernel regulates the rate at which aggregates grow in solution and it is an essential component of the Smoluchowski equation describing conservation of the aggregate size distribution within the dispersion. The effect of hydrodynamic interactions on the coagulation kernel is two-fold: through the relative diffusivity and through the collision efficiency.

The effect of interparticle hydrodynamic interactions on the relative diffusivity is easily understood by considering the two limiting simulation cases: Brownian Dynamics in which hydrodynamic interactions are neglected, and the RPY simulations in which long-ranged interactions are modeled with high fidelity. When neglecting hydrodynamic interactions, an aggregate of $i$ particles moving with velocity $U$ feels a drag force resisting its motion: $F^H = -6\pi \eta_s a U$. By the fluctuation dissipation theorem [45], the relative rate of diffusion of two such aggregates is:

$$D_{ij} = \frac{kT}{6\pi \eta_s a} \left( \frac{1}{i} + \frac{1}{j} \right).$$ \hspace{1cm} (3.7)

That is, the relative diffusivity is proportional to the sum of the reciprocals of the numbers of particles within the aggregates. This resembles Rouse diffusion in polymer mechanics [46]. If the hydrodynamic model were extended to support inclusion of only near-field hydrodynamic interactions between particles in the aggregates – as with FLD – the same scaling of the aggregate diffusivity would result. Diffusion of aggregates in simulations where hydrodynamic lubrication is the only mechanism for energy dissipation is identical to diffusion in those which neglect hydrodynamic interactions entirely.

In contrast, an aggregate moving with velocity $U$ and made of $i$ particles, which interact via long-ranged hydrodynamic interactions, feels a drag force: $F^H = -6\pi \eta_s \Lambda^{1/d_f} U$ [46]. The quantity $d_f$ is the fractal dimension of the aggregate, and $\Lambda$ is the shape factor or lacunarity of the aggregate, which is proportional to the particle size $a$. In this case, the relative rate
of diffusion of two aggregates is:

\[ D_{ij} = \frac{kT}{6\pi \eta_s \Lambda} \left( \frac{1}{i^{1/d_f}} + \frac{1}{j^{1/d_f}} \right). \]  

(3.8)

Although such a scaling relation cannot be precise for small aggregates, its form suggests the correct physics – that the rate of diffusion scales with the inverse of the physical size of the aggregate. Since \( d_f \geq 1 \) for a physical aggregate, relative diffusion in models that include long-ranged hydrodynamic interactions is substantially faster than in those that neglect them. Comparing with equation (3.7), it is evident that when hydrodynamic interactions are neglected, particles in an aggregate behave as point sources of resistance as though the aggregate had a fractal dimension of just 1. Long-ranged hydrodynamic interactions among particles in an aggregate lead to screening which enhances the rate of aggregate motion.

Recall that the rate of compaction is relatively insensitive to the dissipation mechanism. Therefore, large and highly immobile aggregates modeled in the absence of hydrodynamic interactions will tend to show significant compaction relative to coagulation. This fully explains the observed shift in the percolation line and contact number distributions when comparing the two methodologies. Without hydrodynamic interactions, a dispersion requires deeper quenches or higher particle densities to form large aggregates that percolate and kinetically arrest. In contrast, long-range hydrodynamic interactions lead to aggregates that are highly mobile. As these aggregates become more compact, their fractal dimension increases and they become more mobile still. This feedback promotes coagulation and drives formation of a system spanning network at conditions consistent with experimental observations [66, 71].

The time scale for coagulation is highly sensitive to the long-range hydrodynamic interactions between particles. These interactions screen the drag on individual particles leading to a relative diffusivity that scales inversely with the characteristic length scales, i.e. collision radius of the aggregates: \( a_i = \Lambda i^{1/d_f} \). Direct evidence of aggregate formation prior to gelation is shown in figure 3-8, which depicts a time series of the growth of a gel in the presence of long-ranged hydrodynamic interactions. Percolation is preceded by the formation of many large aggregates containing roughly 20 particles on average. Although colloidal gelation at modest volume fractions has long been viewed from the perspective of spinodal decomposition, the
eventual arrest of the phase separation depends on the inherent dynamics between particles, in this case dictated by long-ranged hydrodynamic interactions. Ultimately, colloidal gelation is driven by cluster aggregation. Models for the spinodal decomposition of binary mixtures have reported similar results regarding the dynamics of phase separation [78].

The large scale structure of these same dispersions is reflected in the fractal (Minkowski-Bouligand) dimension of the gels they form [79]. At the studied concentrations and system sizes, the percolated networks are not true fractals since self-similarity is not realized at all length scales. However, the box counting dimension of these gels for length scales large relative to the particle size and small relative to the size of the periodic box serves as a good indicator of global structure, and is in excellent agreement with the power law scaling of

Figure 3-8: Time series snapshots of a dispersion with $\phi = 15\%$ and $U_A = 5kT$. The formation of aggregates containing roughly 20 particles on average precedes gelation. Color is used to call out monomers, dimers, trimers, each other n-mer, and the system spanning cluster.
the total correlation function, i.e. \( g(r) - 1 \approx r^{1-3/d_f} \) [80]. Figure 3-9 depicts the fractal dimension of gels observed in BD and RPY simulations as a function of volume fraction and attraction strength. A systematic but modest trend towards higher fractal dimension with increasing volume fraction is detectable. More importantly, the fractal dimension of gels formed via BD is typically 15% higher than those formed via RPY simulations at the same conditions.

Even for strongly bonded, concentrated dispersions, \( U_A = 8kT \) and \( \phi = 25\% \) for example, where local structural differences are not observable, the large scale structure as signified by the fractal dimension differs considerably between the two simulation methods. This sensitivity of fractal dimension to hydrodynamic interactions has been noted in various simulations of diffusion limited cluster aggregation [81–83]. The present work indicates that collective motions of aggregated colloids bias the percolated network to lower fractal dimensions even in the case of the strong bonding and high concentration. The fractal dimension of a gel is intimately related to the gel rheology; thus, accurate models of rheological properties will exhibit great sensitivity to the pathway along which gelation proceeds [84,85].

The second effect of hydrodynamic interactions on coagulation is through the collision efficiency. When the range of attraction between aggregates is much smaller than the mean aggregate size, the term \( e^{(U(r)/kT)} \) in equation (3.6) can be replaced by unity. Then, without hydrodynamic interactions, the collision efficiency is \( W_{ij} = 1 \). With only the leading order long-ranged hydrodynamic interactions included, the separation dependent relative diffusivity can be written as [32]

\[
D_{ij}(r) = D_{ij} \left[ 1 - \frac{3\Xi_{ij} a_j}{1 + \Xi_{ij} r} + \frac{\Xi_{ij}(1 + \Xi_{ij}^2)}{1 + \Xi_{ij}} \left( \frac{a_j}{r} \right)^3 \right],
\] (3.9)

where \( \Xi_{ij} = a_i/a_j \). This is an approximation which neglects contributions of shape to the relative diffusivity, but includes the leading order \( 1/r \), Stokeslet, and \( 1/r^3 \), Stokes dipole, contributions for spherical aggregates of finite size. This contribution to the slowing of diffusive motion between two fractal aggregates is an underestimate but always positive, which leads to an integrable kernel for the stability ratio. With these simplifications, the collision efficiency can be fit to within 0.1% by the nearly quadratic function: \( W_{ij} \approx 1.6554 - \)
Figure 3-9: The fractal dimension for gels formed via BD and RPY simulations as a function of volume fraction and strength of interparticle attraction as determined by the box counting dimension and confirmed through the power law scaling of the total correlation function. Error bars represent sample to sample fluctuations over three independently generated instances of each gel.

\[ 0.6554(1 - \Xi_{ij})^{2.15}, \] over the range \( \Xi_{ij} \in [0, 1] \). It takes on a value of unity when \( \Xi_{ij} = 0 \) and increases monotonically to 1.6554... when \( \Xi_{ij} = 1 \).

Thus, long-ranged hydrodynamic interactions between aggregates introduce only a weak multiplicative dependence of the coagulation kernel on the aggregate size ratio through the collision efficiency. This effect biases the rate of aggregation to modestly favor interaction of dislike aggregates. The total coagulation kernel including hydrodynamic effects is larger than that neglecting them for all aggregate sizes when assuming \( \Lambda = a \). In cases where aggregation is reaction limited, rather than diffusion limited, a repulsive interparticle potential must be included in the collision efficiency. Then, hydrodynamic interactions can introduce significant changes to \( W_{ij} \) [86], as also discussed in the next chapter.

The effect of long-ranged hydrodynamic interactions on the rate of aggregation is depicted in figure 3-10, which presents the number of \( n \)-mers with \( n = 2, 3, 4 \) as a function of time for
Figure 3-10: The number density \( n_i = N_i \phi / N 4 \pi a^3 \) of \( n \)-mers with \( n = 2, 3, 4 \) as a function of time for \( \phi = 15\% \) and \( U_A = 4kT \) in the absence of hydrodynamic interactions (open symbols) and with hydrodynamic interactions (filled symbols). The dashed and solid lines represent the solution of the Smoluchowski coagulation equation using the diffusivities in equations (3.7) and (3.8), respectively.

\( \phi = 15\% \), \( \delta = 0.1 \) and \( U_A/kT = 4kT \) for both simulation methods. The evolution of the \( n \)-mer distribution from solution of Smoluchowski’s coagulation equation using the diffusivities in equations (3.7) and (3.8), assuming \( W_{ij} = 1 \), is presented as well. When long-ranged hydrodynamic interactions are modeled correctly, rapid gelation occurs, favoring fast growth of large clusters \( (n > 4) \) as small aggregates are depleted from solution. In the case that these interactions are neglected, small aggregates \( (n \leq 4) \) form initially and then grow slowly via monomer addition. Coagulation into larger clusters proceeds at a reduced rate and the concentration of small aggregates appears steady.

The solution of Smoluchowski’s coagulation equation displays the same qualitative behavior as found for simulation of the two hydrodynamic models - a gap between the concen-
trations of small \( n \)-mers results from the size dependence of the aggregate diffusivity. The initial stages of gelation are dominated by coagulation of particles in to larger aggregates since compaction and break-up cannot occur without the existence of such aggregates.

For the Smoluchowski model with the BD-like diffusivity of aggregates, the concentration of small aggregates decreases mildly with time as larger clusters are slowly formed through monomer addition. With the RPY-like diffusivity of aggregates, the coagulation equation predicts a stronger decline in the number of small \( n \)-mers as they leverage their mobility to quickly coalesce into system spanning structures. As Smoluchowski’s coagulation equation describes the kinetics of binary aggregation in terms of a mean-field equation in the dilute limit \((\phi \rightarrow 0)\), differences between simulation results and solutions to this equation are natural. It is possible to construct self-consistent closures to improve on these limitations and obtain more accurate predictions \([87,88]\). However, Smoluchowski’s simple model is sufficient to explain the effect of hydrodynamic interactions on cluster aggregation observed in simulations.

### 3.5 Conclusion

In this chapter we have demonstrated a minimal discrete element model for colloidal gelation and highlighted the critical effect that long-ranged hydrodynamic interactions have on the structure and kinetics of the gelation process. Although more sophisticated hydrodynamic models such as Stokesian Dynamics can be deployed for particulate simulations, the Rotne-Prager-Yamakawa mobility used here is sufficient to capture both the shift in the percolation line and the reduction in mean contact number seen in experiment and more complicated hydrodynamic models when compared to models that neglect interparticle hydrodynamics.

While lubrication and intermediate-range hydrodynamic interactions have been neglected, the simulations employing RPY hydrodynamics are consistent with experimental results for depletion gels, and provide strong evidence that aggregate diffusion rates are key for determining the terminal state in a dispersion of attractive particles. These results confirm what has long been suspected - that there is an intimate connection between the gelation of colloids with short-range attraction and phase separation. A thermodynamic driving force
for aggregation is required as gels form in the two-phase region. The graph theory methods introduced here to analyze gel networks and used throughout this thesis should also be powerful for identifying and characterizing meso-scale structures from real-space position data that dictate the mechanics of other networked colloidal materials, like capillary suspensions and particle networks at interfaces.

Subsequent chapters will employ this same simple model of the physical processes governing gelation to extend investigations to other interparticle potentials (chapter 4), larger system sizes (chapters 6-9), and dispersions deformed by different driving forces (chapters 7-9). For instance, using the RPY method the formation of a streamer driven by back-flow of the solvent through the percolated structure can be carefully studied, a physical effect that cannot even be realized in Brownian Dynamics simulations. The ability to extend the model to other dynamic phenomena makes the RPY approach likely the most parsimonious for colloidal gelation.

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Chapter 4

Enhanced Gelation Through Hydrodynamic Interactions in the Presence of a Repulsive Barrier

4.1 Introduction

A number of studies have focused on the role of the interparticle potential in determining the structure and dynamics in a diverse array of practical and model colloidal dispersions that gel [9]. Experiments have provided evidence that in colloidal dispersions where particles simultaneously experience a short range attraction and a screened electrostatic repulsion, particles tend to form aggregates, whose shape and size depend sensitively on the balance between attraction and repulsion [20,90,91]. Reported observations range from stable, freely diffusing aggregates of particles [92, 93] to colloidal cluster phases progressively evolving toward an arrested state via linear cluster growth followed by percolation [94].

Among the most well-studied cases is a dispersion of colloidal silica in water. Increasing the ionic strength of the dispersion decreases both the range and the magnitude of electrostatic repulsion by reducing the Debye screening length. The electrostatic screening due to added salt results in destabilization of the initially stable dispersion via reaction limited cluster aggregation (RLCA) and space-filling network formation [95–97]. RLCA involves the
passage of particles across a repulsive energy barrier leading to a bonding probability on approach of less than unity. Thus particles may explore and approach multiple bonding sites before aggregating permanently, thereby slowing the rate of coagulation considerably [98].

These cluster phases appear not only in model spherical dispersions, but also in protein solutions, in the limit of low salt concentration, where the origin of arrested states that hinder protein crystallization is of great interest [92, 99]. Therefore the focus of fundamental research in both experiments and simulations has been on gelation in systems where short-ranged attractions, which favor particle aggregation, are complemented by weak long-ranged repulsions, which provide stabilization against gelation.

Figure 4-1: Outcome of aggregation in BD and RPY simulations with $\phi = 15\%$, $U_A = 6kT$, $\delta = 0.1$, $A = 8kT$ and $\kappa_{DA} = 0.8$ after 1000 bare diffusion times. Left: without hydrodynamic interactions, right: with long-ranged hydrodynamic interactions. The right sample is a highly fractal network forming a system spanning gel while the left is a dispersion of repulsive aggregates. Color is used to call out monomers, dimers, trimers, and other n-mers, as well as the system spanning cluster.

As we have shown in the previous chapter, the gelation kinetics and the gel microstructure depend strongly on energy dissipation mechanisms within the gel. We demonstrated that long-ranged hydrodynamic interactions are an essential physical feature of gelation in dispersions of attractive colloids with no long-ranged repulsion. A simple macroscopic model explained why Brownian Dynamics (BD) simulations fail to produce gels consistent with experimental measurements while simulations with long-ranged hydrodynamic interactions reproduce experimentally observed structure and kinetics with great fidelity. In summary,
aggregates coagulate via collective diffusion – a transport process whose rate is strongly enhanced by long-ranged hydrodynamic interactions between the particles. At the same time, aggregates are driven to become more compact by transitioning through various metastable, compact states – a process that is only mildly slowed by hydrodynamic interactions. When the dispersion becomes thermodynamically unstable and the rate of coagulation exceeds the rate of compaction, a system spanning gel results. Thus, long-ranged hydrodynamic coupling plays a key role in the formation of weak gels.

The focus in this chapter is on colloidal dispersions where a short-ranged attraction is complimented by a long-ranged repulsion (SALR) modeling screened Coulomb interactions. The role of screened electrostatic repulsions in aggregating materials has been well-studied in molecular dynamic simulations [100]. For certain screening lengths and interaction strengths, disordered, arrested states self-assemble [101] and gelation may occur as the result of arrested micro-scale phase separation [102].

For the case of SALR dispersions, there are at present three studies [67, 69, 103] that have investigated the role of hydrodynamic interactions, albeit for small system sizes. In one study [67], only short-ranged hydrodynamic lubrication was included in the model, and little difference with respect to freely draining BD was observed. In the second study [69], the Stokesian Dynamics (SD) method was used for the hydrodynamic model, and a significant shift in the percolation line was observed. In the latter work, the strength of the short-ranged attraction and the long-ranged repulsion were held fixed while screening length and particle volume fraction were varied. The authors were unable to provide a systematic explanation for the differences observed with respect to freely draining BD. Finally, in a small scale numerical study on alumina suspensions [103], Stochastic Rotation Dynamics (SRD) was used to include hydrodynamics and the authors also reported a significant shift in the percolation line. These studies together with the results from chapter 3 suggest that hydrodynamic lubrication is unimportant and that long-ranged hydrodynamic interactions are the culprit for such dramatic differences in the observed percolation boundary for SALR dispersions.

We continue the study of the role of hydrodynamic interaction in colloidal gelation and now focus on the interplay of a repulsive barrier, which hinders aggregation, and collective
diffusion, which enhances it. This chapter is organized as follows. Section 4.3.1 discusses the significant disparities between BD simulations and ones using the Rotne-Prager-Yamakawa (RPY) tensor as the hydrodynamic model. For a large range of conditions the freely draining simulations predict that dispersions self-assemble into spherical clusters stabilized by mutual repulsion, while we observe quasi one-dimensional cluster growth followed by percolation in the RPY simulations. The percolation boundary in the RPY simulations agrees with experimental observations [94]. In 4.3 three different conditions are studied in depth to understand the effect of long-ranged hydrodynamics on both the structure and dynamics of gels. We study the local bonding geometry around each particle, the structure factor, and complement these static measurements with the mean-squared displacement and the coherent and incoherent scattering functions. The effect of long-ranged hydrodynamic interactions on the aggregation kinetics of SALR dispersions are analyzed in 4.4. The chapter concludes with a discussion on the necessity of models that account for collective hydrodynamic behavior for studying both limiting forms of colloidal gelation.

4.2 Simulation details

The details of the simulation methodology are discussed in chapter 2. In summary, in BD simulations the approximation of hydrodynamic mobility is configuration independent, and all particles in a solvent of viscosity $\eta_s$ have the identical Stokes mobility $1/6\pi\eta_sa$, which defines the single particle diffusion time scale: $\tau_D = 6\pi\eta_s a^3/kT$. The RPY tensor is an improved approximation with high computational efficiency, which accounts for the far-field translation-force coupling between particles.

SALR particle dispersions with radius $a$ were simulated with and without hydrodynamic interactions at 5 volume fractions: $\phi = 5\%, 10\%, 15\%, 20\%$ and $25\%$. The strength of the interparticle attraction, $U_A$, was varied relative to the thermal energy $kT$, and the range of the interparticle attraction was restricted to interparticle separations smaller than $2a(1+\delta)$, with $\delta = 0.1$. The characteristic screened electrostatic repulsion between charged colloids in an ionic solvent was modeled using the familiar Yukawa form [8]. For all colloidal dispersion considered in this work the parameters were kept constant at $A = 8kT$ and $\kappa_D a = 0.8$. 

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corresponding to typical conditions observed in experiments with PMMA colloids in organic solvents [92, 94]. Depending on the the value of $U_A$, this repulsion leads to a barrier of $\sim 1 - 2kT$ (see figure 4-2). Simulations were run for an initial $10^2\tau_D$ with $U_A = 0$ to ensure thermal equilibration to an initial electrostatically stabilized state, and for subsequent $10^3\tau_D$ with the attractive interactions to generate the gels. The number of particles used in the simulations was $N = 8,000$ throughout, where no system size effects were evident. As discussed in chapter 3, this suggests that percolation in our simulations is independent of system size and occurs when the rate of coagulation of aggregates exceeds the rate of cluster compaction.

### 4.3 Results

Under many equivalent conditions, the RPY simulations result in arrested networks with pore sizes significantly smaller than the periodic simulation domain, while BD simulations result in a phase of dispersed, repulsively stabilized aggregates (see figure 4-1). BD simulations that failed to gel, were run an additional $10^4$ bare diffusion times to confirm that no percolation
occurs. Details of how the gelled state is identified have been described previously [89](see also appendix A). In short, the dispersion is considered a gel, when a cluster that percolates across all the periodic simulation boundaries is detected. That is, if the largest cluster in the simulation box does not connect with its copies in the periodic images, then the configuration is assumed to be non-percolating.

4.3.1 The phase diagram of attractive dispersions with a repulsive barrier

The phase diagram determined from BD and RPY simulations are depicted in figure 4-3. To identify the phase boundaries, we vary $U_A$ in $0.2kT$ increments. No system wide percolation and hence gelation is observed at the lowest volume fraction studied. The repulsive barrier causes the particles to form spherical clusters - the thermodynamic ground-state for small clusters [100]. This configuration allows the particles to maximize distance to other aggregates and suppresses gelation. At higher particle concentrations, the RPY simulations consistently exhibit gelation at lower strengths of attraction than those where hydrodynamic interactions were neglected. Additionally, the gelation threshold shifts to considerably smaller attractions strengths as $\phi$ is increased. In contrast to the case of purely attractive particles, where the gap between the percolation thresholds in RPY and BD was roughly $1kT$ at volume fractions of 10% and greater, in SALR dispersions this gap increases to more than $4kT$ at 10%. A recent mean-field kinetic model of gelation also provides an estimate of the percolation boundary [104]. Like the RPY simulations, this model seeks to correctly account for the collective dynamics of particle clusters during gelation and appears consistent with experiments.

Gelation in systems where short-range attractions are complemented by weak long-ranged repulsions have also been carefully investigated experimentally [90–93]. Also shown in figure 4-3 is an experimentally determined percolation boundary dividing a fully ergodic cluster fluid and a nonergodic gel [94]. In their work Campbell and coworkers estimate that the particles experience a long-ranged screened Coulombic repulsion with $\kappa_D a = 0.78$ and a potential at contact such that $A \sim 7 - 8kT$. Their observed phase boundary is in good
agreement with our RPY simulation results. For many equivalent conditions, in RPY simulations we observe percolation of one-dimensional aggregates as in the experiments, while BD simulations produce a set of repulsively stabilized cluster phases. Still, at low particle concentrations and for weak attractions, the repulsive interactions dominate and a cluster fluid is observed in both simulation methods, consistent with the experiments.

The findings of Campbell and coworkers suggest that kinetic arrest occurs via one-dimensional cluster growth and percolation above a critical volume fraction. Below this cutoff
particles form stable, equilibrated clusters near their thermodynamic ground state [94]. Work by Mossa et al. [100] has shown that for specific choices of the parameters of the repulsive potential, the ground-state energy per particle has a minimum for highly anisotropic linear cluster shapes. At low packing fractions in the thermodynamic limit a "glass" of repulsive clusters forms. Subsequently it was shown that for specific choice of the Yukawa parameters and above a volume fraction of 10%, one-dimensional growth of the clusters is followed by dynamic arrest [101]. A branching mechanism helps build a connected three-dimensional network.

These mechanisms appear to be reproduced in our simulations with hydrodynamic interactions. Indeed, as we will show, RPY dynamics produce structures with lower fractal dimension when compared to BD simulations. When long-ranged hydrodynamic interactions are correctly accounted for, collective diffusion is anisotropic. This leads to a preferred aggregation direction and enhanced coagulation rate thereby accelerating the thermodynamically preferred one-dimensional cluster growth [100].

However, there is a discrepancy between experiment and RPY simulations at larger volume fractions and weak attractions where we only observe percolation above $\sim 4kT$ while in reality gels are observed for even weaker attractions. This difference might be due to acknowledged experimental uncertainties in the precise strength and exact form of both parts of the interaction potential. Additionally, the Yukawa model might fail to capture the many-bodied nature of the screened, but still long-ranged electrostatic interactions at higher volume fractions. Furthermore, the kinetics of the gelation process will be influenced by higher order hydrodynamic multipoles at large volume fractions.

In order to better understand the effect of long-ranged hydrodynamic interactions on gel structure and dynamics, we carefully analyze three particular conditions using both simulation methods. We keep the following parameters fixed: $\phi = 15\%, \delta = 0.1, A = 8kT, \kappa_D a = 0.8$, and observe the effect of changing the strength of the short-range attraction from $U_A = 3kT$ to $6kT$ and $10kT$. Note, this contrasts with the work of Cao and Morris [97], in which the strength of the attraction was held fixed, but the range of the electrostatic repulsion was varied.
4.3.2 Particle localization and spatial correlations

We characterize the average single-particle dynamics using the particle mean squared displacement (MSD)

$$\langle (\Delta r(t))^2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} (\mathbf{x}(t) - \mathbf{x}(0)) \right\rangle,$$

which we plot in figure 4-4 for the three cases studied. All dispersions exhibit the expected diffusive behavior at short times. For $U_A = 3kT$ no gelation is observed and as such the single particle motion is always diffusive. The two simulation methods are essentially indistinguishable. Because aggregation is minimal, differences in the short- and long-time self-diffusivity are not observed. When the strength of attraction is increased to $U_A = 6kT$, the MSD is fundamentally different. The RPY dynamics enhance collective motion of aggregates and the measured MSD is larger as compared to the BD simulation at early times. As no percolation occurs in the BD case, but instead the ground-state aggregates move independently, the MSD continues to grow diffusively at long times. In comparison, the RPY simulations result
in a percolated network, and a pronounced plateau in the MSD is observed. There appears a corresponding localization length $l$ [74] reminiscent of caging in the dynamics of dense glasses [105]. In the gel this localization is a consequence of the particles being constrained by bonding within the percolating structure.

For the highest attraction strength we observe dynamic arrest for both BD and RPY. However, the time scale for arrest is quite different due to hydrodynamic coupling between the particles. At short times, the MSD is again larger for the RPY simulations, where particle localization occurs after $\sim 30\tau_D$, forming a pronounced plateau. In contrast, localization occurs over shorter length scales and the system is not fully arrested even after $10^3\tau_D$ in BD simulations. In both cases the plateaus indicate a smaller $l$ when compared to that measured with $U_A = 6kT$. The deeper quench reduces particle mobility. As we only simulate particle dynamics over three decades in time, we cannot observe significant network restructuring and corresponding long-time diffusion in these strong gel networks as reported elsewhere [74].

The static structure factor $S(q)$, as defined in equation (3.1), measures spatial correlations between particle positions over distances proportional to $\sim 2\pi/q$. We use $S(q)$ to characterize the structure of the network forming in the colloidal dispersions over a broad range of length scales. In figure 4-5 we plot $S(q)$ for dispersions with $U_A = 6kT$ and $10kT$ at several points in time.

For the shallow quench, $S(q)$ in BD is essentially featureless, with only the nearest neighbor peak observable. At long times we observe the growth of a peak indicative of larger correlated length scales corresponding to isolated clusters of several particles. These elongated aggregates do not percolate. In contrast, in the RPY simulation the system percolates as the particles aggregate quite rapidly. After just $10\tau_D$ a low-$q$ peak is detected that grows significantly with time. This peak is indicative of the system spanning network present in the dispersion.

For $U_A = 10kT$ differences in the structure factor persist. While we observe the growth of a low-$q$ peak in both BD and RPY over time, the length scale of the correlation is different. Whereas in BD $q_{\text{max}}a \approx 0.4 = 2\pi/l$, the peak shifts to $q_{\text{max}}a \approx 0.3$ in RPY in agreement with the localization lengths inferred from the MSD results. Hence while both dispersions are percolated, the characteristic length scale of the gel in RPY is larger. The network has
Figure 4-5: Static structure factor in BD and RPY simulations of an attractive dispersion with $U_A = 6kT$ (top) and $U_A = 10kT$ (bottom), $\delta = 0.1$, $\phi = 15\%$, $A = 8kT$ and $\kappa_D a = 0.8$ at four different points in time: $t/\tau_D = 10, 10^2, 5 \times 10^2$ and $10^3$. For clarity, a constant vertical offset of 3 units was added between structure factors of the two simulation methods. Error bars represent sample to sample fluctuations over five independently generated instances.

fewer branching points and exhibits a preferred one-dimensional growth. This difference should therefore also be reflected in the fractal dimension $d_f$.

The fractal dimension of a gel can be a useful indicator of its large scale structure. We again apply the fixed-grid box counting technique to determine the fractal (Minkowski-Bouligand) dimension of the percolated structure $d_f$ [79]. In figure 4-6 we report the fractal dimension of SALR gels observed in BD and RPY simulations as a function of attraction.
strength for three different volume fractions.

Figure 4-6: The fractal dimension of gels formed in BD and RPY simulations as a function of attraction strength at three volume fractions. $d_f$ is determined by the fixed-grid box counting technique and the power law scaling of the total correlation function at $t = 10^3\tau_D$. Error bars represent 95% confidence intervals for five independently generated instances for each gel.

For all $\phi$ the fractal dimension of gels formed via BD is considerably higher than that formed via RPY simulations at the same conditions. Such a sensitivity of fractal dimension to hydrodynamic interactions has been noted in various simulations of diffusion limited cluster aggregation [81,83]. It has been established that collective motions of aggregated colloids bias the percolated network to lower fractal dimensions even in the case of strong bonding and high concentration. Our latest results now suggest that collective motion plays an equally important role in reaction limited aggregation where the terminal structures can display marked global differences depending on the hydrodynamic model. Even for strong attractions where the systems gel with both methods, the RPY gel structure exhibits a preferential growth direction indicated by the lower $d_f$. It appears, hydrodynamic interactions favor one dimensional cluster growth, a mechanism for gel development discussed previously [100,106]. For $\phi = 15\%$ we find a modest increase in $d_f$ with increasing attraction strength in the case
of RPY. In BD we do not observe gels at a sufficient number of conditions to draw similar conclusions. At volume fractions of 20% and 25% \(d_f\) appears to be largely independent of attraction strength, as local particle crowding facilitates dynamic percolation.

### 4.3.3 Microstructure and local order

To assess microstructural differences we investigate the distributions of the rotationally invariant bond-order parameters \(q_j(i)\) and \(\hat{w}_j(i)\) (with \(j = 4\) and \(6\)) [107], quantitative measures of the local bond topology and symmetry around particle \(i\). These distributions provide a sensitive description of the local environment and correlation of interparticle bonds (figure 4-7 and 4-8). Careful analysis of the \(\hat{w}_6\) distribution facilitates the detection of tetrahedral order as opposed to cubic symmetries [108] in colloidal dispersions. Such analysis has been used in the past to quantify the formation of Bernal spirals in experiments [94]. Also shown in figures 4-7 and 4-8 are the experimentally measured bond-order distributions of \(q_i\) and \(\hat{w}_i\) for \(\phi = 11\%\) and \(U_A = 11kT\) [94]. The distributions of the strong gels compare very well with the experiment, especially with respect to the degree of tetrahedral symmetry observed. We find that once gelation occurs the local bond order of the particles in the network strands is essentially the same in both simulation methods. However, the crucial difference as found earlier lies in the conditions at which these gelled strands form.

At the weakest attraction strength, where a single fluid phase is observed in both BD and RPY simulations, the bond-order parameters appear identical. These values for the parameters reflect a limited amount of tetrahedral symmetry and suggest that the particle arrangements within clusters have cubic order. We find many small aggregates containing on the order of 10 particles. For \(U_A = 6kT\), the BD case continues to exhibit limited tetrahedral symmetry (\(\hat{w}_6\) has a peak close to zero) and reduced cubic symmetry, i.e. a smaller average value of \(q_4\) and \(q_6\), suggesting less compact aggregates. In contrast, for RPY dynamics at the same conditions, the peaks in \(q_6\) and \(q_4\) decrease, while the maximum in \(\hat{w}_6\) shifts to more negative values. The particles lose cubic symmetry and the particles in the gel strands develop greater tetrahedral symmetry, similarly to experiments.

In the strong gels (\(U_A = 10kT\)) the local orientational order is essentially identical in BD and RPY simulations. The gels exhibit limited cubic symmetry and significant tetrahedral
Figure 4-7: $q_4$ and $q_6$ bond-order distributions in gels formed via BD and RPY simulations for the three particle dispersions at $U_A = 3kT$, $6kT$ and $10kT$ with $\delta = 0.1$, $\phi = 15\%$, $A = 8kT$ and $\kappa Da = 0.8$ at $t = 10^3T_D$. Error bars represent sample to sample fluctuations over ten independently generated instances. Also shown are experimental results for $\phi = 11\%$ and $U_A \approx 11kT$ [94].

order. While at large attractions the microstructures formed appear less sensitive to hydrodynamic flows, our $S(q)$ measurements described above indicate that correlation on large length scales in the network are significantly different. Our findings suggest that long-ranged hydrodynamic interactions are key in controlling the kinetics of gelation and hence determine under what conditions gels form. Once dispersions undergo percolation, the local structure around particles is dictated by the depth of the quench and the network strands are similar to the thermodynamically predicted ground-state structure of the Bernal spiral [101].

4.3.4 Relaxation dynamics revisited

To study the dynamics of the SALR dispersions we analyze the spatial dependence of the single particle and collective motion as before for purely attractive systems. The incoherent scattering function, $F_S(q,t)$ and the coherent scattering function, $F(q,t)$, (see (3.2) and
Figure 4-8: $\hat{w}_4$ and $\hat{w}_6$ bond-order distributions in gels formed via BD and RPY simulations for the three particle dispersions at $U_A = 3kT$, $6kT$ and $10kT$ with $\delta = 0.1$, $\phi = 15\%$, $A = 8kT$ and $\kappa_D a = 0.8$ at $t = 10^3\tau_D$. Error bars represent sample to sample fluctuations over ten independently generated instances. Also shown are experimental results for $\phi = 11\%$, $U_A \approx 11kT$, $A \approx 7 - 8kT$ and $\kappa_D a \approx 0.8$ [94].

(3.3)) measure the time correlation in single particle displacements and the collective dynamics of the particles, respectively, over a length scale proportional to $2\pi/q$ and a time lag $t$. Both can be inferred from the intensity autocorrelation function accessible in light scattering experiments. The decay of the correlations from their initial plateau is indicative of network restructuring and relaxation. As before, we fit the data with a stretched exponential: 

$$\exp[-(t/\tau_q)^\beta],$$

where $\tau_q$ is the structural relaxation time and $\beta$ is a stretching exponent. $F_S(q,t)$ and $F(q,t)$ for two sets of conditions in BD and RPY simulations, averaged over five independent instances, are shown in figures 4-9 and 4-10 as a function of the normalized lag time $t/\tau_q$ for a set of wave vectors. For both simulation methods the relaxation times are found to scale as $\sim q^{-2}$ – the single-particle as well the collective modes exhibit diffusive particle dynamics.

$\beta$ is strongly dependent on the shape of the distribution of relaxation modes, wider distributions leading to lower exponents. We report the stretching exponents $\beta_S$ and $\beta_C$.
for incoherent and coherent scattering respectively, in figure 4-11. Note that our results at low \( q_a (\ll 0.3) \) values are inconclusive due to our current inability to probe the dynamics accurately on such large length and time scales.

Considerable differences in single and collective dynamics are exhibited by the two hydrodynamic models. For \( U_A = 6kT \) in BD, decay of the scattering functions is rapid at all wavelengths. Since there is no kinetic arrest the relaxation time of the system is much shorter than in the other cases discussed. Stretched exponent values of \( \beta_S \approx \beta_C \approx 0.6 - 0.7 \) over all length scales indicate a uniform sub-diffusive behavior due to the presence of long-ranged repulsive interactions. In the absence of percolation there is no dominant length scale. At
The coherent scattering function $F(q,t)$ for BD and RPY gels of $\phi = 15\%$, $\delta = 0.1$, $A = 8kT$, $\kappa_D a = 0.8$ and $U_A = 6kT$ and $10kT$ for selected wave vectors $q$ at $t = 5 \times 10^2 \tau_D$. For clarity, a constant vertical offset of 0.3 units was added between sets of $F(q,t)$. The dashed lines present the trivial exponential $\exp\left(-t/\tau_q\right)$ to emphasize the compressed and stretched nature of the scattering function decay. Sample to sample fluctuations over five independently generated instances correspond to deviations of $\pm 2\%$ - error bars not shown. Inset: the characteristic relaxation time $\tau_q$ as a function of $q$ for the four different dispersions - colors are the same as in the main plot.

The same condition in the RPY case the dispersion percolates. Hence the single particle and collective relaxation times significantly increase (see insets in figures 4-9 and 4-10). $\beta_S$ decreases sharply from $\sim 0.8$ for small wave vectors (as expected from single particle diffusion) to $\sim 0.45$ at larger $q$. This reflects a broad relaxation spectrum over short length scales that is indicative of network restructuring. A similarly stretched decay of $F(q,t)$ at large $q$ suggests that the long-ranged hydrodynamic interactions promote cooperativity that enhances relaxation in the gel.

For the case of $U_A = 10kT$, both with and without long-ranged hydrodynamics, single-particle and collective motion is noticeably suppressed and exhibits signs of percolation as
Figure 4-11: Exponent $\beta$ of $F(q, t)$ (coherent, top) and $F_s(q, t)$ (incoherent, bottom) of BD and RPY gels with $\phi = 15\%$, $\delta = 0.1$, $A = 8kT$, $\kappa_D a = 0.8$ and $U_A = 6kT$ and $10kT$ for selected wave vectors $q$ at $t = 5 \times 10^2 \tau_D$. Sample to sample fluctuations were measured over five independently generated instances.

seen for the $6kT$ gel in RPY. The BD case stands in stark contrast to the weaker dispersion as it is now kinetically arrested. $F_s(q, t)$ for BD and RPY exhibit very similar stretching exponents, $\beta_s$ decaying from unity at large length scales to values of $\sim 0.4 - 0.5$ at large $q$. As expected, for large quenches beyond the percolation boundary, single-particle motion is dictated by the thermodynamics, not long-ranged hydrodynamics and the two different kinetic models produce only small disagreements. In contrast we observe statistically significant differences in $F(q, t)$ and $\beta_C$ and considerably faster relaxation times for RPY (see insets) attributable to the role of long-ranged hydrodynamic interactions in the collective motion of the gel.
4.4 Aggregation kinetics in attractive dispersions with a repulsive barrier

As established in the previous chapter, the kinetics of the transition on quenching from the dispersed to the condensed state are controlled by two competing processes: compaction of individual aggregates that seeks to maximize interparticle contacts and minimize surface energy, and coagulation of different aggregates. This is true whether a long-ranged repulsion is present or not. At the onset of aggregation, thermodynamics will dictate the formation of small anisotropic clusters in their ground-state [100]. When compaction is much faster than coagulation, the particle aggregates will grow isotropically, and the electrostatic repulsion will maximize the separation between these aggregates. When compaction is much slower than coagulation the network will be space spanning and have high surface area. The onset of gelation is observed when the rate processes of compaction and coagulation are comparable.

As recently discussed elsewhere [104, 109] bond-breakup and dissociation can also play an important role during gelation, especially for weaker attractions. However, just like for compaction, these rate processes are also set by thermal barrier hopping of particles within an aggregate between different meta-stable configurations [76]. As shown in the previous chapter, for a particle bound by depletion interactions strong enough to produce a percolated state, bond-breakup should occur at a vanishingly small rate and increment slightly the effective compaction rate [89, 110]. Ultimately, as seen for the case of phase separation of binary mixtures [78], the process of colloidal gelation is dominated by cluster aggregation.

In SALR dispersions, due to the repulsive barrier, most particle orientations will not result in a bonded state. In fact repeated bonding attempts are necessary before aggregation can proceed and there is a considerable waiting time between coagulation events of clusters. Hence clusters are more likely to compact and find their local thermodynamic ground-state before kinetic arrest occurs. The relative rates of the competing physical transport processes and consequently the percolation line are incredible sensitive to the long-ranged hydrodynamic interactions, suggested by the significant gap between RPY an BD gelation boundaries seen in figure 4-3.
Furthermore, differences in the preferential growth direction of clusters are inherent in the different hydrodynamic models employed in the two simulation methods. Consider the coagulation kernel introduced previously in (3.5). It describes the rate at which two anisotropic aggregates containing $i$ and $j$ particles collide and cohere within the dispersion $K(i, j) = 4\pi(a_i + a_j)D_{ij}/W_{ij}$, where, $a_i$ is the collision radius of an aggregate with $i$ particles, $D_{ij}$ is the relative rate of bare diffusion between aggregates of size $i$ and $j$, and $W_{ij}$ is the collision efficiency [77]. Hence the rate of coagulation is proportional to both the collision cross section and the rate of diffusion of the aggregates along the direction in which they approach each other. The cross section of the aggregate is independent of the dissipation mechanism - in general $a_i$ will be of the size of a particle as bonding events occur pairwise between two particles within coagulating aggregates. However, the rate of diffusion differs considerably between the two hydrodynamic models. In addition, without long-ranged hydrodynamic interactions, $D_{ij}$ is isotropic. Thus, in BD growth along a preferred direction is thermodynamically driven via modulation of the collision efficiency.

In contrast, in models including long-ranged hydrodynamic interactions, $D_{ij}$ is larger than in BD simulations and highly anisotropic [32], with a higher mobility along the major axis of the aggregate. The translational diffusivity of a single cluster containing $N$ particles...
scales as $N^{-1/d_f}$ in the RPY simulations while in BD simulations the translational diffusion of a cluster is significantly slower: $\sim N^{-1}$. In principle, clusters can approach each other at any angle relative to their major axes, however there are three principal configurations that can occur, as shown in figure 4-12a)–c). Let the normalized rate of collision for scenario a) be $K$. Clusters diffuse approximately twice as fast along their major axis than perpendicular to it [32]. Hence the collision rate in b) will be twice as high as before, $2K$. Finally, in c) where both clusters diffuse along their major axes, the normalized collision rate will be $4K$, i.e. four times higher than for the perpendicular approach.

Long-ranged hydrodynamic interactions have an additional role, facilitating the aggregation between two elongated bodies in low-Reynolds-number flow. Originally analyzed in terms of increased reaction rates between enzymes and ligands, it is now established that hydrodynamic interactions create a steering torque when two aggregates move towards each other [111], leading to preferential alignment on approach, as highlighted in figure 4-12d). This rate process is quantified by the rotational diffusivity of the cluster. In BD, the rotational diffusivity, $D_R$, scales as $\sim N^{-(d_f+2)/d_f}$, and $D_R \sim N^{-3/d_f}$ in RPY simulations. Thus, for large aggregates, the rates of reorientation due to diffusion and steering torque are enhanced by long-ranged hydrodynamic coupling.

The relative amounts of elongated structure formation produced in each simulation can be explained by three rate processes: the rate of cluster compaction, the rate of cluster aggregation, and the rate of cluster reorientation. In BD simulations, translational diffusion of clusters is isotropic, and for large clusters, rate of aggregation greatly exceeds the rate of cluster reorientation via diffusion or steering torque. Percolation and kinetic arrest only occurs when compaction rates are low relative to the rate of aggregation such as when the interparticle attractions are strong or the particle number density is sufficiently high for clusters to interpenetrate. Additionally, the contrast in the aggregation and reorientation rates favors more compact percolating structures when they form.

For the RPY model, the rates of aggregation and reorientation of large clusters are comparable. Thus, the steering torque works in concert with translational diffusion to bring clusters together along their major axes, which promotes elongated structural growth. Occasionally, we observe clusters binding transversely which forms branching points in the net-
work. Hence long-ranged hydrodynamic interactions favor anisotropic growth and enhances kinetics favoring percolation of colloidal dispersions stabilized by long-ranged electrostatic repulsion.

In summary, there are three well-known kinetic consequences of long-ranged hydrodynamic interactions that we postulate and that explain the position of the percolation boundaries observed in simulations of SALR dispersions:

1. The collective diffusion of aggregates is strongly enhanced by long-ranged hydrodynamic interactions between the particles. In contrast the rate of aggregate compaction, which involves bond dissociation and bond rearrangement of individual particles on the aggregate surface, is only mildly slowed by hydrodynamic flows.

2. Anisotropic clusters diffuse anisotropically when the long-ranged hydrodynamic interactions are properly incorporated. Consequently, aggregation of clusters along their major axes is kinetically favored when compared with lateral aggregation.

3. Long-ranged hydrodynamic interactions enhance the response to the steering torque that guides approaching clusters into a low energy and strongly bonded conformation. This steering torque ensures a preferential growth direction of the clusters and reduces the fractal dimension of the resulting gel.

We cannot separate or distinguish these effects from one another in the RPY simulations since they arise from the same physical origin, the $1/r$ scaling of the hydrodynamic mobility coupling of widely separated colloidal particles.

Recall that in BD large aggregates will be highly immobile [89]. The formation of aggregates is fast initially as single particles combine to form larger clusters. However, coagulation slows on growth of the mean cluster size because diffusive motion of the clusters is artificially suppressed in BD. Without the significantly larger relative diffusivity produced by long-ranged hydrodynamic interactions, the dispersion stabilizes in a state for which long-ranged repulsion between compact aggregates hinders further aggregation and percolation. In comparison, a simulation that accounts for the long-ranged hydrodynamic interactions promotes aggregates that are highly mobile. This leads to rapid relative diffusive motion.
of clusters at all scales and a considerably increase in the aggregation rate. This contrast fully explains the observed shift in the percolation line when comparing the two simulation methods.

4.5 Conclusion

The investigation presented here has shown that long-range correlations and particle cooperativity near the gelation boundary are sensitive to hydrodynamic interactions between colloids and hence aggregate diffusion rates. These dynamics ultimately determine the terminal state of an aggregating colloidal dispersion by influencing the location of the percolation line. We have presented a detailed study on the influence of the choice of hydrodynamic model on the structural and dynamic properties of a colloidal dispersion in which the short-ranged attraction is complemented by a screened electrostatic repulsion.

We not only observe a significant shift in the percolation boundary, but also find considerable differences in the terminal structure and particle dynamics for deep quenches where gelation is observed for both simulation methods. While the local microstructure is set by the thermodynamics of the dispersion, hydrodynamic interactions fundamentally determine the global structure of the gel. Kinetic arrest in RPY simulations proceeds through preferential one-dimensional cluster growth. We have explained these findings in terms of a simple model for anisotropic translational and rotational diffusion of elongated aggregates at low-Reynolds-numbers. Whereas in BD, coaggregation rates among clusters are only mildly anisotropic, in RPY long-ranged hydrodynamic interactions will enhance alignment and aggregation along the major axes of the cluster, resulting in percolation and network development.

The large discrepancies observed between BD and RPY simulations for purely attractive dispersions is not an isolated example. Modeling the correct kinetics – by correctly accounting for hydrodynamic interactions – is fundamentally imperative in order for simulations to match experimental observations. Analytical theories capable of explaining these differences are needed to provide further insight. Comprehensive comparison among BD, RPY and SD simulations on a large scale are necessary for a definitive assessment of the role of short-ranged lubrication forces and to identify more subtle effects of hydrodynamic forces on gel
Application of computational design for engineering particle assembly requires simulations that can account for all relevant physical transport processes and produce experimentally observed materials. Long-ranged hydrodynamic forces are necessary in discrete element models studying the terminal state of gels built from colloidal dispersions. These past two chapters of this thesis have provide ample evidence that the structure of the arrested gel is sensitive to the hydrodynamic flows around diffusing particles and aggregates. We have presented and discussed the performance of a minimal hydrodynamic model that appears to efficiently capture the kinetics of aggregation leading to faithful reproduction of experimental observations. The results in the following chapters make the case that any computational scheme with the aim to predict bulk properties of these arrested materials accurately, will have to provide a realistic description of the stresses in a relaxing network.

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Chapter 5

The Linear Viscoelasticity of Attractive Colloidal Dispersions

5.1 Introduction

In this chapter we investigate the stress response of a semi-dilute colloidal dispersion subjected to small strain rate linear oscillatory shear in order to predict the linear viscoelastic behavior. The dispersion stress is calculated as a virial expansion in the particle volume fraction, \( \phi \), and maximum rate of strain, \( \dot{\Gamma} \), up to \( O(\phi^2 \dot{\Gamma}) \). The stress response is converted into a complex viscosity describing the intrinsic relaxation time scales in the material. The attractive particle dispersion is characterized in terms of three parameters: The width and the attraction strength at interparticle contact, as well as the ratio of the particle hard core radius to the particle hydrodynamic radius.

The results demonstrate how the strength and range of attraction affects the rheology of an attractive dispersion. The interparticle attraction may reduce or increase the viscosity compared to a dispersion of hard spheres depending on the attractive strength and range. Imposing different values can lead to markedly different viscoelastic spectra. Whereas weak attractions lead to smaller viscosities than those of hard sphere dispersions, strong attractions above a critical value, produce large viscoelastic responses with significant elastic plateaus. Such strong attractions may lead to an unstable dispersion at all volume fractions.

The strength of hydrodynamic interactions is modulated by controlling the limit for
steric repulsion between particles. In the two limiting cases of full and zero hydrodynamic interactions, respectively, the viscoelastic response is shown to be the superposition of the viscoelastic Maxwell mode and the purely repulsive hard sphere response that dominate at low and high shear frequencies respectively. Comparison of our work to previous experimental results demonstrates that our theory is capable of capturing the viscoelastic properties of attractive colloidal dispersions below the gel transition.

The chapter is organized as follows. Section 5.2.1 describes the interactions that govern the behavior of particles in dispersion. Section 5.2.2 details how the microstructure of a colloidal dispersion deforms under small strain rate linear oscillatory shear and derives the resultant deviatoric stress. The results for linear response and the effect of the three parameters are discussed in section 5.3. The article concludes with a discussion of new insights on how to engineer the viscoelasticity of attractive colloidal dispersions.

5.2 Analysis

5.2.1 Particle interactions

The Noro-Frenkel extended law of corresponding states [113] and experimental work on colloidal dispersions [9, 24, 66, 114] suggest that short-ranged interactions all have a quantitatively similar effect on the phase behavior of dispersions, irrespective of the exact shape of the potential. To allow comparison with many common experiments, the Asakura-Oosawa potential is applied in the model [43]. Note that the effective interaction between the colloids as described by the depletion potential is strictly only valid as long as the depletants are Boltzmann distributed [7]. Driven far from equilibrium this pair potential might not be accurate. However, as this work only considers small, linear perturbations, it is justified to assume that the pair-wise attraction between particles of hard sphere radius \( b \) is well described by the depletion potential, which is characterized by the potential range \( \delta \), and the attraction strength at interparticle contact \( U(r = 2b) = U_A \). The interparticle potential nondimensionalized on the thermal energy scale, \( kT \), is denoted \( \tilde{U} \) throughout. Using the
reduced second virial coefficient:

\[ B_2^* = -\frac{3}{b^2} \int_0^\infty \left( e^{-U(r)/kT} - 1 \right) r^2 dr, \]  

we are able to compare a dispersion with the depletion potential to other short-ranged attractions and draw more general conclusions about attractive dispersions:

As discussed previously, phase diagram of a system of colloids having short-ranged attractions [7] displays a wide region of coexistence between a dilute liquid and a solid crystalline phase. For strong attractions, the metastable fluid within the coexistence region experiences fluid-fluid spinodal decomposition followed by the onset of crystallization. However, this spinodal decomposition is often interrupted or masked as a percolation transition occurs between transient cluster and transient network forming regions. In the absence of percolation, kinetic arrest during phase separation can lead to cluster growth. Below the spinodal line and left of the percolation transition, in the presence of a thermodynamic barrier, the dispersion can remain in a metastable state as a colloidal dispersion [9]. Despite being metastable, short-range attractions stabilize the fluid and its properties can be studied, both experimentally and with the help of thermodynamic models. [23].

Under flow, fluid streamlines in a viscous medium distort in the presence of particles and lead to hydrodynamic (non-conservative) forces that can generate large stresses in the colloidal dispersion [115]. In this chapter the effect of hydrodynamic interactions is accounted for via the excluded annulus model. Two length scales characterize the particles in the mono-disperse dispersion: \( b \), the thermodynamic radius at which the repulsive hard sphere interaction occurs, and \( a \), the hydrodynamic radius at which the solvent must satisfy the no-slip condition. This one parameter model describes the effect of repulsion, with solvent filling the gap between \( a \) and \( b \) that is not accessible to depletants and other particles [116,117]. Hence the particles experience the depletion potential for interparticle separations \( 2b \leq r < 2b(1 + \delta) \). The strength of the hydrodynamic interactions is given by the ratio \( \tilde{b} = b/a \). For \( \tilde{b} \to \infty \), there are no hydrodynamic interactions between particles and the dispersion is freely draining, just as in a Brownina Dynamics simulation. When \( \tilde{b} = 1 \), it is possible for the hydrodynamic radii of the particles to approach asymptotically close to
contact and the flow of fluid in the thin gap between particles generates large stresses [32]. The lubrication forces slow the relative flux and retard motion to restore the equilibrium distribution. Throughout this work, all parameters are considered to be independent of the value of \( b \).

Our model is constructed in terms of the volume fraction of colloidal particles \( \phi = 4\pi n a^3 / 3 \) and is evaluated in the semi-dilute limit (\( \phi \ll 1 \)) to order \( \phi^2 \), meaning that only pair interactions are considered. A colloidal dispersion is intrinsically viscoelastic as Brownian motion aims to restore the equilibrium distribution of the particles. Diffusion sets the inherent relaxation time scale of the dispersion [45]. However, in the semi-dilute limit, it is the relative diffusion of particle pairs that controls the relaxation and drives the restoring flow. Correspondingly the characteristic diffusivity \( D = kT / (3\pi \eta_s a) \) is twice the Stokes-Einstein diffusivity.

### 5.2.2 The dispersion microstructure in small strain rate linear oscillatory shear

The complex, non-Newtonian behavior of a dispersion can be understood by considering the colloidal dispersion microstructure and the perturbations to it under flow. At equilibrium, the microstructure is isotropic. When sheared, the conservative and non-conservative forces result in local anisotropic perturbations in the microstructure [115, 118, 119]. Figure 5-1 depicts the quadrupolar pattern in the microstructural perturbation typical of linear viscoelasticity in colloidal dispersions. For steady flow, regions of higher and lower particle pair density delineate compressional and extensional quadrants. As the shearing frequency increases, the out-of-phase component of the structure takes on the opposite sign of the in-phase component but with different magnitude. Therefore the phase angle of the perturbation is always less than ninety degrees, and the stress in the dispersion is out-of-phase with the strain. In the case of hard sphere dispersions, regions of high and low particle number density are found along the compressional and extensional axes, respectively. This is also true for weak attractive potentials, which exert forces that aid particle arrangement along the compressional directions of the shear field.
On the other hand, in the case of strong attraction potentials, closely neighboring particles effectively form dumbbells that rotate to align with the flow field [120]. The oscillatory shear aims to separate these particles while the attractive forces between neighbors now oppose this flow, leading to increased viscous dissipation. The quadrupolar microstructural perturbation is effectively inverted, displaying an enhanced particle number density along extensional, and a reduced probability of finding particles along compressional lines. It is of great interest to understand how this inversion in microstructure with increasing attraction strength takes place, what the perturbation at this inversion point looks like and what non-Newtonian response, if any, such an attractive colloidal dispersion exhibits.

Figure 5-1: Distribution of neighboring particle number density around a particle for the case of a hard sphere (left) and for a large attractive depletion potential (right) with an attraction range \( \delta = 0.1 \) and full hydrodynamic effects. The data is the solution of the Smoluchowski equation (5.2) for small, linear perturbations. The circle in middle of each plot corresponds to the excluded volume of particles. Lighter, red shades reflect positive values of the microstructural perturbation and hence increased particle number density, while darker, blue shades reflect the opposite. Neutral green reflects zero perturbation. The absolute scale is arbitrary and chosen to maximize visibility.

The colloidal dispersion's nonequilibrium microstructure and transient perturbations to it under oscillatory shear are of key interest. Ultimately, the stress in a dispersion depends on these perturbations, given by the radial pair-distribution function, \( g(r, t) \), that characterizes the structure of the fluid and governs the statistics of particle separation. It describes the probability of finding a neighboring particle at a distance \( r \) from the center of a reference
particle at time $t$. The equilibrium distribution, $g^{eq}(r)$ is given by the interaction potential through the Boltzmann distribution: $g^{eq}(r) = \exp(-U(r)/kT)$. The radial distribution function obeys the Smoluchowski equation, a conservation equation balancing fluxes of advection, attraction due to short-ranged forces, and diffusion [115],

$$\frac{dg}{dt} = -\cos(\omega t) \nabla \cdot g \mathbf{U}_r + \nabla g \cdot \mathbf{D} \cdot \nabla \log(g/g^{eq}).$$

(5.2)

The relative velocity between particles due to the imposed shear is $\mathbf{U}_r(r) = \hat{\mathbf{\Gamma}} \cdot \mathbf{r} - \mathbf{H}_a(r) : \mathbf{E}$ where $\hat{\mathbf{\Gamma}}$ is the strain rate amplitude tensor and $\mathbf{E}$, the symmetric rate of strain tensor, is the symmetric part of $\hat{\mathbf{\Gamma}}$. The boundary conditions are dictated by the decay of the microstructure to its equilibrium state at a large separation ($r \to \infty, g(r) = g^{eq}(r)$) and by enforcing a no flux boundary condition at contact ($r=2b$):

$$\frac{r}{|r|} \cdot [g \cos(\omega t) \mathbf{U}_r - \mathbf{D} \cdot g \nabla \log(g/g^{eq})] = 0.$$  

Solutions of the Stokes equations around a pair of particles yield the specific form of the relative diffusivity, $\mathbf{D}(r)$, and advection arising from hydrodynamic interactions between a pair of particles in shear flow, $\mathbf{H}_a(r)$. These tensors may be expanded into orthogonal contributions [118] as:

$$\mathbf{D}(r) = G(br)\hat{\mathbf{r}} + H(br)(\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}),$$  

(5.3)

$$\mathbf{H}_a(r) = r[A(br)\hat{\mathbf{r}} + B(br)(\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}})]\hat{\mathbf{r}}.$$  

(5.4)

Here $G(br)$ and $A(br)$ are scalar hydrodynamic functions that represent the relative diffusion and relative advection of a particle pair along the line of centers between the particles. Similarly, $H(br)$ and $B(br)$ represent the same perpendicular to the line of centers. In contrast to the bare linear flow, $\mathbf{H}_a(r)$ is not divergence free. Therefore the divergence of the velocity field is:

$$\nabla \cdot \mathbf{U}_r = -\nabla \cdot (\mathbf{H}_a : \mathbf{E}) = -W(br)(\hat{\mathbf{r}} \cdot \mathbf{E} \cdot \hat{\mathbf{r}}) = -[r \frac{dA(br)}{dr} + 3(A(br) - B(br))](\hat{\mathbf{r}} \cdot \mathbf{E} \cdot \hat{\mathbf{r}}).$$  

(5.5)
The following scales are chosen by which the equations are made dimensionless: \( r \) is rescaled by \( b \), \( U_r \) is rescaled by \( \hat{\Gamma} b \), the characteristic flow velocity, where \( \hat{\Gamma} = \sqrt{\frac{1}{2} \Gamma : \hat{\Gamma}} \). \( D(r) \) is rescaled by \( D \). This yields two dimensionless groups in the governing equation: 

\[
\alpha = \frac{\omega b^2}{D}, \quad \text{the oscillation frequency made dimensionless on the diffusive time scale; and} \quad Pe = \frac{\hat{\Gamma} b^2}{D}, \quad \text{the Péclet number characterizing the strength of flow relative to thermal forces on the particles.}
\]

For weak flows (\( Pe \ll 1 \)) the deformation must be linear in \( Pe \) and the radial distribution function can be expressed as a small perturbation, \( f(r, t) \), from the equilibrium distribution:

\[
g(r, t) = g_{eq}(1 - Pe \cdot E \cdot \hat{\Gamma} f(r, t)) \quad [121].
\]

Substituting this expression into the Smoluchowski equation (5.2) yields the governing equation for the perturbation function and associated boundary conditions:

\[
\frac{df}{dt} = -\frac{\cos(\alpha t) \nabla \cdot g_{eq} U_r}{g_{eq}} + \left( \frac{\nabla \cdot g_{eq} D \cdot \nabla f}{g_{eq}} \right), \quad (5.6)
\]

\[
r \to \infty, f = 0,
\]

\[
r \to 2, \frac{r}{|r|} \cdot [\cos(\alpha t) U_r (1 + Pe f) - D \cdot \nabla f] = 0.
\]

The perturbed microstructure, \( f(r, t) \), is expanded as a Fourier series in the driving frequency \( \alpha \)

\[
f(r, t) = \sum_{n=-\infty}^{\infty} e^{i\alpha t} f_n(r). \quad (5.7)
\]

For a real valued function such as the perturbed microstructure, \( f_{-n}(r) = f^*_n(r) \), with \( * \) indicating the complex conjugate. Therefore there is no need to solve for modes with \( n < 0 \). As Swan et al. [122] have shown, for vanishing Péclet number and assuming a regular expansion in \( Pe \), the first mode, \( f_1 \) is of \( \mathcal{O}(1) \), while higher order harmonics are of \( \mathcal{O}(Pe) \) or lower. Therefore the general linear response equations are recovered exactly by \( f_1 \) alone. The perturbed microstructure is written as a simple Fourier sum,

\[
f(r, t) = f_1(r, \alpha)e^{i\alpha t} + f_1^*(r, \alpha)e^{-i\alpha t}. \quad (5.8)
\]

The Smoluchowski equation governing the microstructural response takes on the form of an
ordinary differential equation,

\[ i\alpha f_1 = \frac{1}{2} \left( - \left( 1 - A(\dot{b}r) \right) r \frac{d\dot{U}}{dr} + W(\dot{b}r) \right) - G(\dot{b}r) \frac{d\dot{f}_1}{dr} + \frac{1}{r^2} \frac{d}{dr} \left( r^2 G(\dot{b}r) \frac{df_1}{dr} \right) - H(\dot{b}r) \frac{6}{r^2} f_1, \]

(5.9)

with

\[ \left( 1 - A(\dot{b}r) \right) + G(\dot{b}r) \frac{df_1}{dr} = 0, \]

as \( r \to 2 \) and \( f_1 = 0 \) when \( r \to \infty \). An analytical solution for the microstructural perturbation is intractable. Instead, the governing equations were solved numerically using a finite difference and collocation scheme for boundary value problems.

5.2.3 The deviatoric dispersion stress

Under shearing flow, two contributions to the deviatoric stress arise: hydrodynamic stresses due to the non-deformability of the particles, and thermodynamic stress from resistance to distortion of the microscopic structure caused by the restoring effects of interparticle forces and Brownian motion. The interaction potential therefore contributes both in indirect and direct ways to the deviatoric stress of the colloidal system. Indirectly, by augmenting the equilibrium distribution of particles, \( g^\alpha \). Directly, by generating additional thermodynamic stresses that aid or oppose the movement of particles in the flow field.

The deviatoric stress in a colloidal dispersion deformed linearly is given by:

\[ \Sigma(\alpha) = 2\eta_s \dot{\Gamma} \cos(\alpha t) E + \phi \dot{\Gamma} (S^H + S^B + S^P), \]

(5.10)

where the first term represents the solvent phase stress and the three components proportional to the volume fraction of particles, are the deviatoric particle phase stress contributions, specifically: the hydrodynamic stresslet, \( S^H \), the Brownian stresslet, \( S^B \) and the interparticle stresslet, \( S^P \) [118]. In the linear response limit, these three contributions depend
linearly on the microstructural perturbation \([121]\):

\[
S^H = 2\eta_s E \cos(\alpha t) \left( \frac{5}{2} + \frac{5}{2} \phi + \frac{15}{2} \phi \hat{b}^3 \int_2^\infty \left( K(\hat{br}) + \frac{2}{3} L(\hat{br}) + \frac{2}{15} M(\hat{br}) \right) g^{eq}(r) r^2 dr \right),
\]

(5.11)

\[
S^B = 2\eta_s E \frac{9}{40} \phi \hat{b}^5 \int_2^\infty W(\hat{br}) f(r, t) g^{eq}(r) r^2 dr,
\]

(5.12)

\[
S^P = 2\eta_s E \frac{9}{40} \phi \hat{b}^5 \int_2^{2(1+\delta)} \left( 1 - A(\hat{br}) \right) f(r, t) \frac{g^{eq}(r)}{dr} r^3 dr
\]

\[
= 2\eta_s E \phi \left( \frac{9}{5} \hat{b}^5 \left( 1 - A(2\hat{b}) \right) g^{eq}(2) f(2, t) \right) - \frac{9}{40} \phi \hat{b}^5 \int_2^{2(1+\delta)} \left( 1 - A(\hat{br}) \right) f(r, t) g^{eq}(r) \frac{dU}{dr} r^3 dr
\]

(5.13)

The hydrodynamic functions, including \(L(\hat{br}), L(\hat{br})\) and \(M(\hat{br})\) that describe stresses generated by hydrodynamic interactions among a pair of particles in an extensional flow field, encountered in the equations above are well known \([32,119,123]\) and depend only on the dimensionless quantity \(\hat{br}\). When the particles are widely separated, \((\hat{br} \to \infty)\), and when they are nearly touching, \((\hat{br} \to 2)\), these functions have well defined asymptotic representations. Analytical solutions and asymptotic forms of the hydrodynamic functions are used as done previously by Swan and coworkers \([122]\).

Having decomposed the microstructural perturbation, \(f(r, t)\), into a finite sum of Fourier coefficients, the same is done for the stresslets that depend linearly on this perturbation. The obtained Fourier coefficients are linearly proportional to the harmonics of the microstructural deformation \([122]\), where for \(\dagger=\{H,B,P\}\):

\[
S^\dagger = S^{\dagger, \infty} + \sum_{n=-\infty}^{\infty} e^{in\alpha t} S^{\dagger, n},
\]

(5.14)
To describe the general linear response, again only $O(1)$ terms are kept in the Fourier sum:

$$S_{H, \infty}^{\alpha} = 2\eta_s E \cos(\alpha t) \left( \frac{5}{2} + \frac{5}{2} \phi + \frac{15}{2} \phi \hat{b}^3 \int_2^{\infty} \left( K(\hat{b}r) + \frac{2}{3} L(\hat{b}r) + \frac{2}{15} M(\hat{b}r) \right) g^{eq}(r)r^2 dr \right),$$

(5.15)

$$S_B^P = 2\eta_s E \frac{9}{20} \phi \hat{b}^5 \int_2^{\infty} W(\hat{b}r) f_1(r, \alpha) g^{eq}(r)r^2 dr,$$

(5.16)

$$S_1^P = -2\eta_s E \left( \frac{9}{20} \phi \hat{b}^5 \int_2^{2(1+\delta)} \left( 1 - A(\hat{b}r) \right) f_1(r, \alpha) \frac{g^{eq}(r)}{dr}(r^3 dr) \right).$$

(5.17)

The component of the stress independent of the microstructural deformation, the hydrodynamic stresslet arises because the particles are rigid and distort the fluid streamlines. This contribution is entirely Newtonian and reflects the viscous dissipation in an equilibrium dispersion.

For microstructural perturbations at asymptotically high frequency ($\alpha \to \infty$) with any finite Péclet number, the extent of microstructural deformation is vanishingly small. The overall dispersion stress is

$$\Sigma_\infty = 2\eta_s \cos(\alpha t) \hat{\Gamma} E + \phi \hat{\Gamma} S^H.$$  

(5.18)

Figure 5-2 presents the $O(\phi^2)$ increase in viscosity for attractive colloidal dispersions. The effect of attraction range and strength is captured in a single parameter through the second virial coefficient. In the undeformed state, hydrodynamic interactions among the particles enhance the viscosity of the attractive colloidal dispersion.

It is the existence of interactions among the colloidal particles due to the distorted microstructure that yield the non-Newtonian properties. The focus is on the stress that arises only from $f(r, t)$ and is therefore a function of the frequency of shear [124],

$$\Delta \Sigma(\alpha) = \Sigma(\alpha) - \Sigma_\infty.$$  

(5.19)

This yields an expression for the reduced complex viscosity of the colloidal dispersion due
to the deformation of the microstructure. Both the in-phase and out-of-phase components of the viscosity have two contributions. The first component is a result of Brownian forces aiming to restore equilibrium. The other originates from the depletion potential acting between particles. The sign of both contributions to the viscosity depends on whether the Brownian motion and the short-ranged attraction aids or resists the alignment of particles with the flow field.

\[
\eta' - \eta'_\infty = \eta'_B(\alpha) + \eta'_F(\alpha) = \frac{9}{20} \int_2^\infty W(r) r^2 g^q(r) \Re \{f_1(2, \alpha)\} \, dr \quad \text{and} \quad \frac{9}{20} \int_2^{2(1+\delta)} g^q(r) \frac{dU}{dr} r^3 \Re \{f_1(r, \alpha)\} \, dr, \quad (5.20)
\]

\[
\eta'' = \eta''_B(\alpha) + \eta''_F(\alpha) = \frac{9}{20} \int_2^\infty W(r) r^2 g^q(r) \Im \{f_1(2, \alpha)\} \, dr \quad \text{and} \quad \frac{9}{20} \int_2^{2(1+\delta)} g^q(r) \frac{dU}{dr} r^3 \Im \{f_1(r, \alpha)\} \, dr. \quad (5.21)
\]
5.2.4 In the absence of hydrodynamic interactions

In the case of \( \hat{d}r \to \infty \), when hydrodynamic interactions are negligible, the hydrodynamic functions take on finite values: \( G = H = 1 \), \( A = W = 0 \), and the relative velocity between particles is now \( \mathbf{U}_r(r) = \dot{\mathbf{r}} \cdot \mathbf{r} \). The differential equation for \( f_1(r, \alpha) \) is of the form

\[
i\alpha f_1 = -\frac{1}{2} \frac{d\hat{U}}{dr} - \frac{d\hat{U}}{dr} \frac{df_1}{dr} + \frac{2}{r} \frac{df_1}{dr} + \frac{d^2 f_1}{dr^2} - \frac{6}{r^2} f_1,
\]

(5.22)

with the boundary condition at \( r = 2 \)

\[1 + \frac{df_1}{dr} = 0,
\]

and as \( r \to \infty \) \( f_1 \to 0 \). In this limit the \( \mathcal{O}(1) \) contributions to the deviatoric stress are

\[S^{H, \infty} = 2\eta_s E \cos(\alpha t) \left[ \frac{5}{2} + \frac{5}{2} \phi \right],
\]

(5.23)

\[S^B_1 = 0,
\]

(5.24)

\[S^P_1 = 2\eta_s E\phi \left[ \frac{18}{5} g^{eq}(2) f_1(2, \alpha) - \frac{9}{20} \int_2^{2(1+\delta)} g^{eq}(r) \frac{d\hat{U}}{dr} r^3 f_1(r, \alpha) dr \right].
\]

(5.25)

In the absence of hydrodynamic lubrication forces, particles can now come into full contact. Both contributions to the complex viscosity originate from the interparticle potential. The first is due to the hard sphere like repulsion of particles at contact and the second results from the depletion potential between the particles,

\[\eta' - \eta'_\infty = \eta'_P(\alpha) + \eta'_P(\alpha) = \frac{18}{5} g^{eq}(2) \mathbb{R} \{ f_1(2, \alpha) \} - \frac{9}{20} \int_2^{2(1+\delta)} g^{eq}(r) \frac{d\hat{U}}{dr} r^3 \mathbb{R} \{ f_1(r, \alpha) \} dr,
\]

(5.26)

\[\eta'' = \eta''_P(\alpha) + \eta''_P(\alpha) = \frac{18}{5} g^{eq}(2) \mathbb{M} \{ f_1(2, \alpha) \} - \frac{9}{20} \int_2^{2(1+\delta)} g^{eq}(r) \frac{d\hat{U}}{dr} r^3 \mathbb{M} \{ f_1(r, \alpha) \} dr.
\]

(5.27)
5.2.5 Low and high frequency asymptotic limits

For $\hat{b} \to \infty$ perturbation analysis permits the study of the asymptotic forms of the microstructure and elucidates the dominant contributions to $f_1$ that determine $\eta^*$ at low and high $\alpha$, respectively. In the limit $\alpha \ll 1$ a regular perturbation expansion in the small parameter $\alpha$, $f_1 = f^{(0)} + \alpha f^{(1)}$, for equation (5.22) yields two equations of $\mathcal{O}(1)$ and $\mathcal{O}(\alpha)$:

\begin{align*}
0 &= -\frac{1}{2} \frac{d\hat{U}}{dr} - \frac{d\hat{U}}{dr} \frac{df^{(0)}}{dr} + \frac{2}{r} \frac{df^{(0)}}{dr} + \frac{d^2 f^{(0)}}{dr^2} - \frac{6}{r^2} f^{(0)}, \quad (5.28) \\
if^{(1)} &= -\frac{d\hat{U}}{dr} \frac{df^{(1)}}{dr} + \frac{2}{r} \frac{df^{(1)}}{dr} + \frac{d^2 f^{(1)}}{dr^2} - \frac{6}{r^2} f^{(1)}, \quad (5.29)
\end{align*}

with the boundary conditions:

\[ \frac{df^{(0)}}{dr} = -1 \text{ at } r = 0, f^{(0)} \text{ as } r \to \infty \text{ and } \frac{df^{(1)}}{dr} = 0 \text{ at } r = 0, f^{(1)} = 0 \text{ as } r \to \infty. \]

Solving for $f^{(0)}$ and $f^{(1)}$ and using equations (5.26) and (5.27) yields first order approximations to $\eta' - \eta'_\infty$ and $\eta''$ respectively, as $f^{(0)}$ is purely real and $f^{(1)}$ is purely imaginary.

For high frequencies, $\alpha \gg 1$, equation (5.22) admits a solution, the outer solution $f^{(0)}_O$, that scales as $\alpha^{-1}$:

\[ if^{(0)}_O = -\frac{1}{2} \frac{d\hat{U}}{dr} \alpha^{-1}. \quad (5.30)\]

This first order solution cannot satisfy the no-flux boundary condition at interparticle contact ($r = 2$). In the absence of hydrodynamic interactions, the boundary layer that develops near the particle surface scales as $\alpha^{-1/2}$ with the microstructural perturbation also scaling as $\alpha^{-1/2}$ [124]. To account for this, we introduce the stretched coordinate $w = (r - 2)\alpha^{1/2}$, an order one quantity when $w$ is within the layer, and solve for the perturbation in the boundary layer. In this region and to leading order the inner solution to the perturbation, $f^{(0)}_I$, satisfies the equation

\[ if^{(0)}_I = -\frac{d\hat{U}}{dw} \frac{df^{(0)}_I}{dw} + \frac{d^2 f^{(0)}_I}{dw^2} - \frac{d\hat{U}}{dw}, \quad (5.31)\]
with
\[ i f^{(0)}_I \to -\frac{1}{2} r \frac{d\hat{U}}{dr} \alpha^{-1} \text{ as } w \to \infty \text{ and } \frac{df^{(0)}_I}{dw} = -\alpha^{-1/2} \text{ at } w = 0. \]

Since the boundary layer is thin, the potential is linearized in this region
\[ \frac{d\hat{U}}{dw} \xrightarrow{w \to 0} \frac{3}{4} \phi \delta^{-3} \alpha^{-1} (2\delta \alpha^{-1} - w) = \frac{3}{4} \phi \alpha^{-4} C^{-3} (2C - w). \] (5.32)

As mentioned, two competing length scales characterize the equation that governs the microstructural perturbation. For the case, \( \delta \sim \alpha^{1/2} \), a solution to the perturbation function is only of interest in the region \( 0 \leq w \leq 2C \), within the depletion layer, since outside the depletion layer there is no contribution to the viscosity. The perturbation function within the depletion layer satisfies
\[ i f^{(0)}_{w<2C} = -\frac{d\hat{U}}{dw} \frac{df^{(0)}_{w<2C}}{dw} + \frac{d^2 f^{(0)}_{w<2C}}{dw^2} - \frac{d\hat{U}}{dw} . \] (5.33)

However, \( f^{(0)}_I \) is also non-zero outside the depletion layer and satisfies equation (5.33) with \( \frac{d\hat{U}}{dw} = 0 \). As the perturbation is continuous and smooth for all values of \( w \), including the edge of the depletion layer, this then sets the relation of the function and its derivative at \( w = 2C \) as
\[ \frac{df^{(0)}_{w<2C}}{dw} + \sqrt{i} f^{(0)}_{w<2C} = 0 \text{ at } w = 2C \text{ and } \frac{df^{(0)}_{2C}}{dw} = -\alpha^{-1/2} \text{ at } w = 0. \]

For the case, \( \delta > \alpha^{-1/2} \leftrightarrow \alpha > \delta^{-2} \) the boundary layer is much smaller than the depletion layer, i.e. the potential gradient within the boundary layer is negligible: \( d\hat{U}/dw \ll O(1) \). The microstructural perturbation satisfies the equation
\[ if^{(0)}_I = \frac{d^2 f^{(0)}_I}{dw^2} , \] (5.34)

with
\[ \frac{df^{(0)}_I}{dw} = -\alpha^{-1/2} \text{ at } w = 0 \text{ and } f^{(0)}_I \to 0 \text{ as } w \to \infty, \]

since it is the next term in this singular expansion that matches the outer solution, \( f^{(0)}_O \).
Therefore, the microstructural perturbation in the boundary layer to first order is

\[ f^{(0)}_i = \frac{(1 - i) e^{\frac{1}{2} \sqrt{2} (1+i) \nu}}{\sqrt{2\alpha}}. \]  

(5.35)

5.3 Results

This section is organized as follows. 5.3.1 details the effects of \( U_A \) and \( \hat{b} \) on the steady shear viscosity increase due to the microstructure. In 5.3.2 we analyze the findings on the viscoelastic spectra of attractive colloidal dispersions in the presence of full hydrodynamic interactions and identify a critical potential strength that represents the transition between two markedly different viscoelastic regimes. The results for the special case of \( \hat{b} \to \infty \) are discussed in 5.3.3 and the effects of the strength of hydrodynamic interactions on the complex viscosity are detailed in 5.3.4. Finally, in 5.4 we demonstrate that the viscoelastic spectrum is the result of the superposition of two physical modes and concludes with a discussion on how one can tune the viscoelasticity of an attractive dispersion.

5.3.1 The viscoelastic response at steady shear

The analysis of the behavior of the microstructural perturbation at steady shear \( \eta'_0 - \eta'_\infty \) (where \( \eta'_0 = \eta'(\alpha \to 0) \)) yields initial insights on the effect of hydrodynamic and attractive interaction on the rheology of a colloidal dispersion. Figure 5-3 presents \( \eta'_0 - \eta'_\infty \) as a function of both \( U_A \) and \( \hat{b} \) at a constant attraction range \( \delta = 0.1 \).

For dispersions with full hydrodynamic effects, \( \eta'_0 - \eta'_\infty \) as a function of the contact attraction strength \( U_A \) displays a minimum at a critical value of the attractive potential, \( U_{\text{crit}} \). While the exact value of \( \eta'_0 - \eta'_\infty \) at \( U_{\text{crit}} \) depends on \( \hat{b} \), in general weakly attractive wells yield \( \eta'_0 - \eta'_\infty \) lower than that of hard spheres. This effect is of theoretical interest as it has been interpreted from previous calculations for adhesive spheres that hard sphere interactions define the minimum attainable viscosity for a given dispersion [125]. This is not a numerical artifact, but a result of weak attractive colloidal dispersions being perturbed less by shear than hard sphere dispersions [120].

Concurrently, \( \eta'_0 - \eta'_\infty \) as a function of the hydrodynamic interaction strength goes through
a maximum, the location of which is at $\hat{b} - 1 \sim \mathcal{O}(1)$ for all studied attraction strengths at a constant attraction range. This occurs because of the competition between two different contributions of the interparticle attractive potential to the deviatoric stress of the dispersion. Attractive forces increase the equilibrium distribution of neighbors around the particles and lead to crowding. On the other hand a depletion potential may pull particles away from the extensional and push them together along the compressional axes, thereby relieving stress in the system.

In the following the results for the real, in-phase (fluid like) and imaginary, out-of-phase (solid like) component of the complex viscosity $\eta^*$ are rescaled by $\eta'_0 - \eta'_\infty$ to put the viscoelastic spectra for particles with varying $U_A$ and with different $\phi$ on the same basis for comparison.

### 5.3.2 Viscoelastic spectra of attractive colloidal dispersions

The normalized complex viscosity, $\Delta \eta' = \frac{\eta' - \eta'_\infty}{\eta'_0 - \eta'_\infty}$ and $\Delta \eta'' = \frac{\eta''}{\eta'_0 - \eta'_\infty}$, is plotted in figure 5-4 as a function of the dimensionless frequency, $\alpha$, for a range of attraction strengths $U_A$ at a fixed depletion range, $\delta = 0.1$. Even in the semi-dilute limit, colloidal dispersions
exhibit a distinctly different behavior compared to the viscoelastic response of hard spheres. Depending on the strength of attraction between particles, the qualitative shape of the complex viscosity curves varies.

![Complex Viscosity Curves](image)

Figure 5-4: The normalized linear viscoelastic spectra of semi-dilute attractive colloidal dispersions, $\Delta \eta' = \frac{\eta' - \eta'_\infty}{\eta'_0 - \eta'_\infty}$ and $\Delta \eta'' = \frac{\eta'' - \eta''_\infty}{\eta''_0 - \eta''_\infty}$, are plotted as a function of the dimensionless frequency $\alpha$, with varying $U_A$, fixed attraction range, $\delta = 0.1$, and full hydrodynamic interactions, $b = 1$. The data is normalized by $\eta'_0 - \eta'_\infty$ to put the viscoelastic spectra for particles with different $U_A$ and $\phi$ on the same basis for comparison. These results are derived from (5.20) and (5.21).

For frequencies $\alpha < 1$, the viscoelasticity in the dispersion develops similar to a dispersion of hard spheres: The in-phase contribution is constant with frequency, $\eta' - \eta'_\infty \sim C_1$ while the out-of-phase contribution increases from zero linearly with frequency, $\eta'' \sim C_2 \alpha$, displaying a peak at $\alpha \sim 1$. The theoretical crossover point of the asymptotic behavior of these two contributions defines $\alpha_{\text{cross}}$ and is an intrinsic measure of the time scale of relaxation in the material. The viscoelastic relaxation time of the dispersion is defined as: $\tau_{ve} = \alpha_{\text{cross}}^{-1} = C_2/C_1$.

In the case of weak attractions below the particular potential of $U_{\text{crit}}$ the dispersion exhibits a complex viscosity that is qualitatively similar, but lower than that of hard spheres. This was observed at steady state, $\alpha = 0$, by Bergenholtz and Wagner [120] for square well potentials as well. While the attraction contributes positively to the hydrodynamic stress by
increasing dissipation, this is outweighed by the negative contribution to the thermodynamic stress: The attractive forces push particles together along the compressional and move them apart along the extensional directions, thereby reducing the amount of stress required to maintain the perturbed microstructure. When the attraction between particles is increased and $U_A$ approaches the value of $U_{\text{crit}}$, the peak elasticity shifts to larger frequencies.

For the critical attraction strength $U_{\text{crit}}$ the peak in the elastic component is shifted to a frequency range $\alpha \sim \delta^{-1}$. As figure 5-5 shows, the critical attraction strength produces regions of high and low densities in all quadrants of $g(r)$. While very close to contact the structural perturbation remains positive in the compressional and negative in the extensional quadrant, at larger separations the density distribution is inverted as is the case for higher attraction strengths. Effectively, this leads to markedly smaller stress in the microstructure than for lower or higher $U_A$ and a nearly Newtonian behavior. This produces the lowest magnitude of complex viscosity of all dispersions studied.

\[
U_A = 3kT
\]

Figure 5-5: Distribution of neighboring particle number density around a particle for the case of the critical attractive potential, $U_A = 3kT$ with $\delta = 0.1$ and $b = 1$. The circle in middle of the plot corresponds to the excluded volume of particles. Lighter, red shades reflect positive values of the microstructural perturbation and hence particle number density, while darker, blue shades reflect the opposite. Neutral green reflects zero perturbation. The absolute scale is arbitrary and chosen to maximize visibility.

For stronger attractions, the magnitude of $U_A$ greater than that of $U_{\text{crit}}$, the complex viscosity is higher than for hard spheres and a second peak in $\Delta \eta''$ of larger magnitude than
the first is developing at $\alpha \sim \delta^{-1}$. This overlaps with the first peak and the elastic response now displays a plateau in the range $1 < \alpha < \delta^{-1}$. Essentially, above $U_{\text{crit}}$ the attractive force is large enough to cause the aforementioned inversion in the quadrupolar structure [115]. Along extensional directions in the flow field large attractive forces act to maintain particles close to contact, withstanding separation. Consequently the particle number density along the compressional axis is reduced. Therefore, a larger stress is required to maintain the microstructure under shear, leading to an elevated complex viscosity.

For $\alpha \to \infty$ the microstructural perturbation is restricted to a boundary layer close to interparticle contact [124] and the oscillatory shear only probes the stresses produced in the boundary layer. Here, the effect of weak attractions is a mild perturbation from the hard sphere microstructure and has no marked effect on the viscoelastic spectrum.

However, for potentials deeper than $U_{\text{crit}}$, the rheological response is a result of the interplay of two length scales: the characteristic width of the boundary layer, $\alpha^{-1}$ and the range of the attractive potential, $\delta$. Therefore, contrary to the hard sphere case, where both components of the viscosity decrease with increasing frequency, the complex viscosity for a strong attractive dispersion displays the aforementioned plateau in the extended frequency range near $\alpha \sim \delta^{-1}$. Now the boundary layer is of the same size as the attractive range between neighboring particles. The potential gradient spans the entire layer and stresses are confined to within this layer. Therefore the deformation of the microstructure does work against the full range of the attractive potential. This leads to the observed elastic plateau.

At very high frequencies, the boundary layer is much smaller than the depletion layer, and the change in attractive force over this distance is negligible. The components of the viscosity decrease as $\alpha^{-2}$ and $\alpha^{-1}$ respectively. This produces the expected crossover in loss and storage moduli.

Figure 5-6 plots the results for the viscoelastic relaxation time, $\tau_{ve}$ as a function of contact attraction strength, $U_A$ and attraction range, $\delta$. As described above, in the case of weak attractions, as $U_A$ approaches the value of $U_{\text{crit}}$, the displayed peak elasticity shifts to larger frequencies and the relaxation time of the structure decreases. Small attractive potentials overall decrease the thermodynamic stress in the dispersion and the material’s stress response to shear flow is faster. The minimum in $\tau_{ve}$ is observed for the critical attraction strength
Figure 5-6: Left: The relaxation time $\tau_{ve}$ of semi-dilute attractive colloidal dispersions are plotted as a function of $U_A$, for varying attraction ranges, $\delta$, and for full hydrodynamic interactions, $\hat{b} = 1$. The minimum in the relaxation time occurs for the critical potential strength, $U_{crit}$. Right: When plotted as a function of $B_2^*$, the data collapses onto a single curve and the observed $U_{crit}$ for different $\delta$ correspond to a single value of $B_2^*$.

$U_{crit}$. The markedly smaller perturbation due to the distribution of neighboring particle number density leads to the very fast relaxation of the dispersion. For stronger attractions than $U_{crit}$, the elevated thermodynamic stresses in the microstructure lead to an increase in relaxation time. Additionally, it is found that $\tau_{ve}$ increases as $\delta$ is increased. At a constant $U_A$, an increase in $\delta$ results in greater attractive forces and thermodynamic stresses. These slow the structure’s response to changes in shear flow and increase the relaxation time. When graphing the relaxation time as a function of the reduced second virial coefficient $B_2^*$, which subsumes attraction strength and range in a single parameter, the data collapses very well onto a single curve. This suggests that an increase in the attraction strength and range have similar effects on the viscoelasticity of the dispersion. Intriguingly, the observed $U_{crit}$ values for different $\delta$ correspond to a single value of $B_2^*$, indicating that in fact the minimum in $\tau_{ve}$ and its value is irrespective of the exact potential shape.
5.3.3 Complex viscosity without hydrodynamic interactions

In certain dispersions such as protein aggregate solutions, the colloidal particles experience weak hydrodynamic interactions [126]. It is therefore interesting to investigate the physical behavior of our model colloidal dispersion in the absence of fluid mechanical forces.

Figure 5-7: The normalized linear viscoelastic spectra of semi-dilute attractive colloidal dispersions, $\Delta \eta'$ and $\Delta \eta''$, are plotted as a function of the dimensionless frequency $\alpha$, with increasing contact $U_A$, fixed attraction range, $\delta = 0.1$, in the absence of hydrodynamic interactions, $b \to \infty$. Data is computed from (5.26) and (5.27).

The numerical solution of equation (5.22) for the microstructural perturbation is used to compute the viscoelastic spectrum of the dispersion for a range of $U_A$ and at a fixed $\delta = 0.1$, presented in figure 5-7. There are distinct differences from the hard sphere response, as well as differences when compared to a hydrodynamically interacting dispersion. In the $\alpha \to \infty$ limit, both components of the complex viscosity scale as $\alpha^{-1/2}$. Depending on the strength of the attractive potential, the exact shape of the viscosity curves varies substantially. For weak attractions, the dispersion exhibits a complex viscosity that is qualitatively similar, but lower than for hard spheres. Strong attractions produce an elastic component characterized by two distinct peaks and a trough. This contrasts with the complex viscosity of a dispersion with $b = 1$, where $\Delta \eta''$ displayed an extended plateau after its peak value.

There again exists a range of values of the attractive potential, $0 < U_A < U_{\text{crit}}$, that leads
to lower viscosities than that of the hard sphere dispersion. At a potential equal to $U_{\text{crit}}$ the first peak in the elastic component is shifted furthest in $\alpha$, corresponding to the shortest relaxation time.

![Graph](image)

Figure 5-8: Left: The relaxation times $\tau_{\text{ve}}$ of semi-dilute attractive colloidal dispersions are plotted as a function of $U_A$, for varying attraction ranges, $\delta$, in the absence of hydrodynamic interactions, $\hat{b} \to \infty$. The minimum in the relaxation time occurs for the critical potential strength, $U_{\text{crit}}$. Right: When plotted as a function of $B^*_2$, the data collapses onto a single curve and the observed $U_{\text{crit}}/kT$ for different $\delta$ correspond to a single value of $B^*_2$.

For potentials above $U_{\text{crit}}$ the rheological response is again the result of the interplay of two length scales: the width of the boundary layer that forms at high frequency, $\sim \alpha^{-1/2}$ and the width of the potential well, $\delta$. For $\alpha < 1$ the viscoelastic response arises as the shearing works against the attractive force that resists the separation of particle pairs by the flow field, similarly to the situation with full hydrodynamic effects. This generates a peak elasticity at $\alpha \sim 1$. However, as the frequency is increased further, the microstructural perturbation becomes restricted to a boundary layer close to the particle, which has width proportional to $\alpha^{-1/2}$ [124]. The oscillatory deformation probes the stresses within this boundary layer. Both the viscous and the elastic components of the complex viscosity begin to decline. At higher frequencies where $\alpha \sim \delta^{-2}$ (contrast this with $\alpha \sim \delta^{-1}$ for $\hat{b} = 1$) the boundary layer is of the same size as the width of the potential. As the potential gradient spans the entire boundary layer, the perturbed particles generate stresses across the full range of the attractive force.
This again leads to an increased elastic response such that $\Delta \eta''$ displays a second peak. As $\alpha$ is increased further, the boundary layer is much smaller than the depletion layer and as such the attractive potential produces little stress. There is reduced energy dissipation or storage and the components of the viscosity decrease as $\alpha^{-1/2}$. There is no crossover of $\Delta \eta'$ and $\Delta \eta''$ and the dispersion maintains a liquid-like character.

As was the case with full hydrodynamic effects, the critical value of the potential coincides with the minimum in the characteristic relaxation time of the dispersion, $\tau_{ve}$ (figure 5-8). It also decreases in magnitude with $\delta$. However, in contrast to the full hydrodynamic case, the values of $\tau_{ve}$ are considerably lower. This indicates that in the absence of hydrodynamic interactions, stress relaxation in the system is substantially faster.

When graphing the relaxation time as a function of the reduced second virial coefficient $B_*^2$, the data again collapses very well onto a single curve. Furthermore, as expected, the values $B_*^2$ at the minimum in $\tau_{ve}$ for the two limiting cases of $\hat{b}$ appear to coincide, strongly suggesting that the minimum is thermodynamic in origin and therefore only weakly dependent on the strength of the hydrodynamic interaction. A critical potential strength, marked by $B_*^2 \sim 0.3$, determines the underlying relaxation behavior.

### 5.3.4 Variation in the strength of hydrodynamic interactions

The quantity $\hat{b}$ is the length scale describing the degree of steric repulsion between particles and is experimentally measurable. In many dispersion the hydrodynamic radius $a$ is taken to be nearly identical to the hard sphere radius $b$, i.e. $\hat{b} = 1$. However, in several different colloidal dispersions particles experience a repulsion beyond their hydrodynamic radius so that $b > a$, and the hydrodynamic interactions between colloids are weaken. Steric boundaries created by polymer chains that adsorb on the particle surface act to stabilize many dispersions, but may lead to particles having a thermodynamic radius that extends beyond their hydrodynamic radius [127]. In other situations, colloids may repel electrostatically as with proteins in solutions. These electrostatic forces prevent the protein coils from approaching closely [92, 128]. This behavior is characterized by $\hat{b} \gg 1$.

The relative strength of hydrodynamic interactions has not only a marked effect on the linear viscoelasticity of hard sphere dispersions [121] but also on the rheology of colloidal
Figure 5-9: The normalized linear viscoelastic spectra of semi-dilute attractive colloidal dispersions, $\Delta \eta'$ and $\Delta \eta''$, with $U_A = 5kT$ and $\delta = 0.1$ are plotted as a function of the dimensionless frequency, $\alpha$, for increasing strength of hydrodynamic interactions, $\hat{b}$. The data is normalized by $\eta_0' - \eta'_\infty$ to put the viscoelastic spectra for particles with varying $\hat{b}$ and with different $\phi$ on the same basis for comparison.

dispersions with short-range attractions. Significant differences in the nature of the complex viscosity when $\hat{b} \to \infty$ and $\hat{b} = 1$ were identified in previous sections. In general, with stronger hydrodynamic interactions the dispersion exhibits a reduced complex viscosity, as shown in figure 5-9.

These differences are well displayed in the limit of high frequencies, $\alpha \to \infty$. For strong hydrodynamic interactions, $\eta''(\alpha)$ decays as $\alpha^{-1}$. Lubrication between particles near contact slows their relative diffusion and yields a softer elasticity. The complex modulus, given by $ab^2G^*(\alpha)/kT = i\alpha(\eta^*(\alpha) - \eta'_\infty)/(3\pi\eta_s)$ displays a high frequency plateau for $G'(\alpha)$. Since $\eta'(\alpha)$ decays as $\alpha^{-2}$, the loss and storage moduli exhibit a crossover, producing a solid-like character at high frequencies. In contrast, without hydrodynamic interactions both the real and imaginary parts of the viscosity decay as $\alpha^{-1/2}$ at high frequencies. There is no elastic plateau, nor a crossover in moduli. Without hydrodynamic interactions the particles can freely slide around each other experiencing less retardation.

In their work, Swan et al. [122] observed the same behavior for a semi-dilute hard sphere dispersion under medium amplitude oscillatory flow for $Pe \ll 1$. In the limit of $\alpha \to \infty$,
they reported a transition in the scaling of \( \eta''(\alpha) \) from \( \alpha^{-1} \) to \( \alpha^{-1/2} \) at weak hydrodynamic interactions marked by \( \hat{b} - 1 \sim \mathcal{O}(1) \) (see their Figure 3.). The results in figure 5-9 suggest that in the presence of short-range attractions such a transition occurs for \( \hat{b} - 1 \sim \mathcal{O}(10^{-2}) \), i.e. for stronger hydrodynamic interactions. The interparticle potential aligns particles with the flow field and the relative movement of particles past each other is reduced compared to a hard sphere dispersion. Lubrication forces between particles are therefore smaller, producing less hydrodynamic stress, causing a transition to a markedly different linear viscoelastic response only at smaller \( \hat{b} \), with stronger hydrodynamic interactions.

These results match also well with experimental measurements of the oscillatory rheology in another short-ranged attractive colloidal system, a dispersion of adhesive hard spheres. Woutersen et al. [129] conducted dynamic frequency sweeps on dispersions of silicium-oxide particles over the dimensionless frequency range \( \alpha = 10^{-3} - 10^{3} \). The particles were coated with octadecyl chains, suggesting that the particles used in these experiments had a thermodynamic radius that extended slightly beyond the hydrodynamic radius, diminishing the effects of hydrodynamic interactions (see figure 5-9) and yielding a corresponding value \( \hat{b} \approx 1.08 \). By changes in temperature the second virial coefficient of the attraction between the particles was varied over the range \( B_2^* \approx 0.5 - 2 \), which corresponds to \( U_A \approx 1 - 4kT \) for \( \delta = 0.1 \). The real and imaginary part of the complex viscosity demonstrated the same high frequency decay, scaling with \( \sim \alpha^{1/2} \) as predicted from our linear viscoelastic theory for weak hydrodynamic interactions. However, a complex viscosity lower than that of repulsive hard spheres was not observed in their experiments, possible because the volume fractions studied \( (\phi > 0.4) \) do not correspond to the dilute limit. It is encouraging that the experimental system exhibited the same qualitative relaxation behavior and sensitivity to the attraction strength as suggested by the theory.

### 5.4 The viscoelastic response: a sum of two modes

Figure 5-10 compares the values for the viscous components as obtained by the exact solution of (5.22) and by using the results obtained for the low- and high-frequency asymptotic approximations derived in 5.2.5. Using just the first order term in each expansion is suffi-
cient to capture the viscoelastic behavior of the dispersion in the absence of hydrodynamic effects. The expressions for the complex viscosity in equations (5.26) and (5.27) suggest that the contribution to the viscosity from the perturbation inside the boundary layer is \( \mathcal{O}(\alpha^{-1/2}) \) while the outer solution gives a smaller, \( \mathcal{O}(\alpha^{-1}) \) contribution. Therefore, at very high frequencies both parts of the complex viscosity are expected to scale as \( \sim \alpha^{-1/2} \).

Figure 5-10: Low and high frequency asymptotic approximations to the exact solution of the linear viscoelastic spectrum of a semi-dilute attractive colloidal dispersion, \( \Delta \eta' \) and \( \Delta \eta'' \), as a function of dimensionless frequency, \( \alpha \), for \( U_A = 5kT \) and \( \delta = 0.1 \), in the absence of hydrodynamic interactions, \( \dot{b} \to \infty \). For \( \alpha \to 0 \) and \( \alpha \to \infty \) the first order approximation captures the physical behavior accurately. For frequencies in the range \( 1 < \alpha < \delta^{-2} \) the asymptotic results cannot replicate the transition response exactly.

The asymptotic analysis shows that within the boundary layer the dispersion behaves like a dispersion of hard spheres, not generating any thermodynamic stresses against the attractive force. The qualitative behavior of such a system is well established [121,122,130], our results only differ quantitatively in that the equilibrium distribution of the hard spheres is augmented by the presence of the depletion potential, increasing the density of neighboring particles. For frequencies in the range \( 1 < \alpha < \delta^{-2} \) the asymptotic solution has problems accurately predicting the behavior of the dispersion. This is the region where the transition from the complex viscosity due to stresses probing the interparticle attractive potential,
to the oscillatory shear response of hard spheres occurs. The parameters of the depletion potential determine the exact crossover between these two regimes.

The asymptotic analysis suggests that the rheology of the colloidal dispersion resembles a superposition of two different viscoelastic modes at low and at high frequencies respectively. As mentioned previously, the observed high frequency decay of the viscoelastic spectra is similar to the behavior of hard sphere dispersions. For $\alpha > 1$ it should therefore be possible to fit the viscoelastic spectrum of attractive dispersion to the exact hard sphere dispersion solution using two adjustable parameters:

$$
\eta^*(\alpha) = \exp(-U_{\text{shift}}/kT) \eta_{\text{HS}}^*(\alpha/\alpha_{\text{shift}}). 
$$

(5.36)

As long as $\eta_{\text{HS}}^*$ is known for a specific value of $\hat{b}$, the best-fit values for $\alpha_{\text{shift}}$ and $U_{\text{shift}}$ can be determined for a given $U_A$ and $\delta$.

For the case of a hard sphere dispersion without hydrodynamic interactions under small amplitude oscillatory shear (SAOS), the differential equation describing the perturbation can be solved exactly and the analytical expression for the complex viscosity is well known [124,130],

$$
f_1(2, \alpha) = \left( \left( 1 + i \sqrt{2}\alpha \right)^{-1} + 3 \left( 1 + i \sqrt{2}\alpha \right)^{-2} + 3 \left( 1 + i \sqrt{2}\alpha \right)^{-3} \right) \times \left( 16\alpha^2 \left( 8\alpha^2 - 16(1 + i)^3 \sqrt{\alpha/2} - 18i\alpha - 9(1 + i) \sqrt{\alpha/2} \right)^{-1} \right),
$$

(5.37)

$$
\eta'_{\text{HS}}(\alpha) = \frac{18}{5} \phi^2 \times \Re \{f_1(2, \alpha)\},
$$

(5.38)

$$
\eta''_{\text{HS}}(\alpha) = -\frac{18}{5} \phi^2 \times \Im \{f_1(2, \alpha)\}.
$$

(5.39)

For finite values of $\hat{b}$ only a numerical solution for the hard sphere viscoelastic spectrum is available. This effectively means that only one of the two fitting-parameters can be varied. As the onset of the high frequency decay is set by the range of the attraction, for a given $\delta$ and $\hat{b}$ a fixed value of $\alpha_{\text{shift}}$ is chosen and the best-fit shift in potential, $U_{\text{shift}}$, as a function of $U_A$ is determined.

As figure 5-11 shows, the required shift in potential is positive for values of $U_A$ that are
Figure 5-11: The values of the two shift parameters required to fit the hard sphere viscoelastic response to the high frequency spectra of attractive colloidal dispersions are plotted as a function of $U_A$, for a constant attraction range, $\delta = 0.1$, with full, $b \to 1$ and in the absence of hydrodynamic effects, $\hat{b} \to \infty$. Note, in the presence of hydrodynamic interactions, the frequency shift parameter $\alpha_{shift}$ was kept constant as only numerical results were available for the hard sphere complex viscosity.

below the critical attraction strength, as here the complex viscosity is lower than for hard sphere dispersions. Above $U_{crit}$, the more the contact attraction in the colloidal dispersion is increased, the more negative the value of the shift potential. This is expected, since one effect of the interaction potential on the colloidal microstructure is to increase the equilibrium pair distribution $g^{eq} (r)$ and thus the thermodynamic stresses in the system. The required shift in frequency is necessary as in the presence of attractive interactions, the peak elasticity corresponding to the deformation of the hard sphere microstructure in the boundary layer is shifted from $\alpha \sim 1$ to $\alpha \sim \delta^{-2}$ in the case of $\hat{b} \to \infty$.

For the case of strong hydrodynamic interactions, it is significant that effectively a single parameter $U_{shift}$ is sufficient to reproduce the viscoelastic spectrum of the hard-sphere response. The obtained values for $U_{shift}$ are lower than in the absence of hydrodynamic interactions as in this case the interaction potential has a smaller overall effect on the complex viscosity of the dispersion.

In the low frequency limit ($\alpha < 1$) and for attraction strengths deeper than $U_{crit}$, the
physical response of the colloidal dispersion to small strain-amplitude linear shear resembles the behavior of a spring and a dashpot coupled in series. The straining deformation works to separate particle pairs that form due to the depletion attraction. This behavior is captured by the Maxwell mode characterized by the zero shear viscosity, $\eta_0$, and the relaxation rate, $\alpha_0$ [131]:

$$\eta' = \frac{\eta_0 \alpha_0 \alpha}{\alpha^2 + \alpha_0^2} \text{ and } \eta'' = \frac{\eta_0 \alpha^2}{\alpha^2 + \alpha_0^2}$$

(5.40)

Once the high frequency hard sphere fit is obtained, the difference in the viscosities of the exact solution and the fit over the whole frequency range can be computed. This difference, the escape viscosity, $\Delta \eta_{\text{Escape}}^*$, is due to the stress that is generated by the colloids’ resistance to escaping from the potential well, and is especially prevalent at low frequencies. It is then possible to construct a two parameter best-fit of the Maxwell mode to $\Delta \eta_{\text{Escape}}^*$ for any value of $\tilde{b}$ using (5.40).

![Figure 5-12:](image)

Figure 5-12: The values of the Maxwell parameters required to fit the spectra of attractive colloidal dispersions at low frequencies, are plotted as a function $U_A$, for a constant attraction range, $\delta = 0.1$, with full, $\tilde{b} \to 1$ and in the absence of hydrodynamic interactions, $\tilde{b} \to \infty$.

The results of this two parameter fit are presented in figure 5-12. Essentially there is no difference in the zero shear value $\eta_0$ for different strengths of hydrodynamic interactions. However, as the attraction strength is increased, the steady shear viscosity value of the Maxwell mode increases rapidly. This is again expected as $g^q(r)$ increases with $U_A$ irre-
spective of \( \hat{b} \). The calculated relaxation rate decreases with attraction strength since it was observed that the intrinsic relaxation time of the colloidal dispersion increases as the colloidal particles become more attractive. In general, \( \alpha_0 \) is smaller for larger \( \hat{b} \) as with reduced hydrodynamic interactions the relaxation time of any dispersion increases.

Figures 5-13 and 5-14 show that the resulting viscoelastic response of an attractive colloidal dispersion is the sum of these two physical modes. The delayed onset of the high frequency decay that is observed for all values of \( \hat{b} \) is due to the transition of the microstructural response between the two extremes. As \( \alpha \) increases above 1, the oscillation frequency exceeds the relaxation rate of particles in the attractive potential. However, the developing boundary layer that forms initially is so wide that the particle motion remains sensitive to the gradient in depletion potential.

Our results demonstrate that it is possible to predict and control the viscoelastic spectrum of a colloidal dispersion by engineering the strength of hydrodynamic interactions and the depletion potential. If it is desired to increase the relaxation rate of a dispersion, the strength of the attraction can be decreased or the hydrodynamic interactions increased. Equally, the trough between elastic peaks can be removed by increasing fluid mechanic effects between particles, or the onset of an elastic plateau at high frequencies can be delayed by decreasing the attraction range.

In several applications, such as drug delivery and the development of new pharmaceuticals for injection [5], the developed dispersion is required to exhibit a Newtonian rheology or limited viscoelasticity. We have seen that colloidal dispersions with depletion potentials of strength close to \( U_{\text{crit}} \) exhibit a weakly perturbed microstructure and produce thermodynamic stresses that are lower than for any other dispersion studied. This means, that there is a range of several \( kT \) over which the attraction between colloidal particles in experimental drugs, protein solutions and other colloidal dispersion can be tuned to achieve close to Newtonian fluid-like rheological response.
Figure 5-13: The viscoelastic spectrum of a semi-dilute attractive colloidal dispersion, $\Delta\eta'$ and $\Delta\eta''$ plotted as a function of dimensionless frequency $\alpha$, for $U_A = 5kT$ and $\delta = 0.1$, with full hydrodynamic interactions, $b = 1$. a) The hard sphere viscoelastic spectrum is shifted to fit the data at high frequency ($\alpha \gg 1$). b) Best-fit of the Maxwell mode to $\Delta\eta'_{\text{Escape}}$ at low frequencies ($\alpha \ll 1$). c) The linear superposition of the Maxwell mode and the shifted hard sphere response captures the behavior of the attractive colloidal dispersion over the whole frequency range.
Figure 5-14: The viscoelastic spectrum of a semi-dilute attractive colloidal dispersion, $\Delta \eta'$ and $\Delta \eta''$, plotted as a function of dimensionless frequency $\alpha$, for $U_A = 5kT$ and $\delta = 0.1$, in the absence of hydrodynamic interactions, $b \rightarrow \infty$. 

a) The hard sphere viscoelastic spectrum is shifted to fit the data at high frequency ($\alpha \gg 1$). 
b) Best-fit of the Maxwell mode to $\Delta \eta^\text{Escape}$ at low frequencies ($\alpha \ll 1$). 
c) The linear superposition of the Maxwell mode and the shifted hard sphere response captures the behavior of the attractive colloidal dispersion over the whole frequency range.
5.5 Conclusion

This chapter has presented a detailed analysis of the viscoelastic spectra of a semi-dilute, attractive colloidal fluid below the gel transition undergoing small strain rate linear oscillatory shear. The complex viscosity of the dispersion is calculated using a theory that is exact in the stated limits.

The rheological response is strongly influenced by the strength and range of the attractive potential. There is a clear difference in the linear viscoelasticity for the cases of strong and weak attractions. For a given attraction range a critical potential at contact, $U_{\text{crit}}$, and more generally a critical value of the second virial coefficient is identified that leads to a minimum in the viscoelastic relaxation time of the dispersion. Attraction strengths below $U_{\text{crit}}$ for dimensionless frequencies $\alpha < 1$ produce a stress response that is smaller than that of hard sphere dispersions as the attraction aids particle alignment with the flow field. For $\alpha > 1$ the viscoelasticity of strongly attractive dispersions is characterized by the interplay of two length scales: the developing boundary layer width into which microstructural perturbations are confined, and the range of the attractive potential. In the case of full hydrodynamic interactions this leads to an extended intermediate elastic plateau and to a delay in the onset of a high frequency, power law decay of stress with respect to frequency. In the absence of hydrodynamic interactions a trough develops in the elastic component of the complex viscosity at intermediate frequencies. The depth and width of this trough is controlled by the strength and range of the attraction.

Asymptotic analysis shows that the overall viscoelastic response is essentially the result of two simple physical modes: At low frequencies the shear in the colloidal dispersion works against the interparticle attraction holding particle pairs together, characterized by a Maxwell mode. At high frequencies the system behaves as if it were a dispersion of hard spheres, the attractive potential merely increases the density distribution of particles. The linear superposition of these two modes is in excellent agreement with our exact solution.

Additionally, well characterized effects of hydrodynamic interactions on the viscoelastic spectrum are observed: With strong hydrodynamic interactions, the dispersion exhibits weaker relative viscous and elastic character. Lubrication forces soften the elastic response
and the dispersion exhibits a high frequency elastic plateau. These findings provide strong indication that the fluid mechanics are not only important within colloidal aggregates below the gel transition, but are also central to the mechanical response of kinetically arrested colloidal gels when deformed macroscopically.

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Chapter 6

On the Normal Modes of Weak Colloidal Gels

6.1 Introduction

Normal mode analysis provides a framework for understanding linear excitations of complex systems. The normal modes are those degrees of freedom which, for small perturbations away from equilibrium, do not interact with each other. Each mode oscillates or relaxes independently of the others with its own characteristic frequency or relaxation rate. The distribution of normal mode frequencies or rates, known as the density of states (DOS), is central in the investigation of condensed matter, because it allows one to calculate the specific heat, thermal conductivity, and other thermal and mechanical properties [133]. Normal mode analysis is also a basis for predicting liquid-state dynamics [134], biomolecular relaxation [135], the jamming transition of granular materials [136], and the phonon density of colloidal crystals and glasses [137, 138].

Developed frameworks aim to connect the spectrum of relaxation rates in a soft material to its macroscopic rheological properties [104, 139]. For example, the normal modes of soft materials and their associated DOS may be directly related to their linear viscoelastic response [131]. While significant effort has been devoted to the investigation of the DOS of dense glasses and other disordered colloidal solids [140, 141], much less is known for the case of colloidal gels [142]. While the kinetic pathway leading to arrest is dependent on the
volume fraction, and strength and range of interaction [9], these state parameters are not sufficient to fully characterize the final nonequilibrium state of the gel and its properties. As discussed previously, control of aggregation is critical to many applications so that there is an impetus for developing computational models with better predictive capabilities.

Recent work has used simulations of microstructural dynamics and relaxation to predict mechanical properties of gels [143–147]. Such analysis neglects the role of hydrodynamic coupling of the suspended particles. While for atomic systems the phonon dispersion curve is entirely determined by particle mass and interparticle potentials, due to the relevant length scales in colloidal systems, dissipative interactions mediated by the suspending fluid must be considered [148,149]. Many-bodied hydrodynamic interactions are long-ranged and are therefore usually neglected in large systems. However, we have shown that neglecting long-ranged dissipative coupling in discrete element modeling of gelling systems leads to predictions of structure and dynamics that are at odds with experimental observations [89,112]. Because the modes of relaxation are modulated by the hydrodynamic interactions between particles, the fluid mechanics within a gel must be central to its linear viscoelastic response when deformed macroscopically. Several experiments [137,150] have found that models neglecting hydrodynamic coupling fail to reproduce measured dynamics and friction coefficients. To date, no computational model has been used to investigate the role of hydrodynamic interactions in the mechanical response of arrested colloidal gels and there is thus a need for a hydrodynamic theory to explain the observed relaxation modes [148,151].

Notably, Hurd et al. [152] developed a systematic transport theory for normal modes in a harmonic lattice of colloidal particles immersed in a viscous medium and obtained predictions of the relaxation spectrum for dilute colloidal crystals. For amorphous, space spanning configurations, such as colloidal gels, no analytical models have been constructed.

Here we detail for the first time how hydrodynamic forces in gels built from colloidal spheres affect the normal modes of relaxation and thus their macroscopic mechanical properties. Going beyond the approach taken in the previous chapter, we directly compute and compare the normal mode structure and density of states for relaxation rates in colloidal gels of varying concentration using several different approximations of the hydrodynamic interactions among the colloids. We present a clear case for long-ranged hydrodynamic interactions
playing an essential role in the macroscopic stress relaxation of colloidal gels. In the models developed for the normal modes, the gels are treated as networks of hydrodynamically interacting elements connected via Hookean springs. Thus, the normal modes computed are derived solely from fluctuations and relaxation of this harmonic network structure. The analysis neglects the contribution of excluded volume interactions between the elements to the relaxation process, which are expected to be relevant in highly localized normal modes and at high volume fractions. Also neglected are the breakage and formation of bonds in the network, which contribute to long time aging and restructuring as well as relaxation of tensioned network elements [22]. We test the validity of the harmonic network approximation by comparing the computed relaxation spectrum with stress relaxation in dynamic simulations of shear step-strain in the same gels.

This chapter is organized as follows. In section 6.2 we first present the normal mode analysis of the overdamped momentum balance on colloidal scale particles and investigate the role of both lubrication and long-ranged hydrodynamic interactions, including higher hydrodynamic moments, in the relaxation of gelled structures in 6.3. Section We examine the role of hydrodynamic interactions in setting the characteristic length scale dependence of the normal modes and present the first dispersion relation we are aware of for colloidal networks. In section 6.4 we demonstrate agreement between the asymptotic scaling of the predicted relaxation modulus with that obtained from dynamic simulations and experiments following a step-strain at low and moderate concentrations for particles interacting via more realistic hard sphere and depletion potentials. The chapter concludes with remarks on the consequences of our findings for developing accurate computational tools capable of predicting the mechanical properties of amorphous materials.

6.2 Normal mode analysis

We first generate representative gel configurations by conducting Brownian dynamics simulations with hydrodynamic interactions as described in chapter 2, for \( N = 10^2 - 10^4 \) spherical particles of radius \( a \) with thermal energy \( kT \) in a solvent of viscosity \( \eta_s \) for up to \( 10^4 \) single particle diffusive time steps \( \tau_D = 6\pi\eta_s a^3/kT \). A short-ranged attraction between the
particles given by the Asakura-Oosawa form, is used to drive aggregation [43]. The range is set to $\delta = 0.1$ and its strength is $U_A = 10kT$. For each of the three volume fractions studied, $\phi = 15\%, 30\%$ and $45\%$, we generate 5 independent configurations. At the end of each simulation the sample is gelled, with all particles belonging to a percolating cluster. The static structure factor and representative snapshots of the particle configurations are shown in figure 6-1.

Figure 6-1: Snapshots of the nascent gel structures as generated in simulations with volume fractions (a) $\phi = 15\%$, (b) $\phi = 30\%$ and (c) $\phi = 45\%$. d) Static structure factors $S(q)$ for the three volume fractions studied.

We use particle positions from the terminal states of these simulations to determine the distribution of microscopic relaxation rates and the spatial structure of the normal modes as follows. Evolution of the particle positions, $\mathbf{x}(t) \in \mathbb{R}^{3N}$, is dictated by the overdamped
momentum balance (see 2.2): \[ \frac{dx}{dt} = -M \left( \nabla U - F_B \right), \] (6.1)

where as before $M \in \mathbb{R}^{3N \times 3N}$ is the hydrodynamic mobility tensor, $U$ is the interparticle potential, and $F_B$ is the Brownian force satisfying the fluctuation-dissipation theorem [46]. The kinetically arrested gel state is close to mechanical equilibrium, and the interparticle interactions in this state can be approximated as nearly harmonic. Denoting particle fluctuations about the arrested state, $x_{eq}$, as $\delta(t) = x(t) - x_{eq}$, the time evolution of an average fluctuation is to leading order:

\[ \frac{d\delta}{dt} = -\left( k_0 / (6\pi \eta a) \right) M^{1/2}. \] (6.2)

The tensor $\dot{M}$ is the hydrodynamic mobility in the $x_{eq}$ configuration scaled on the Stokes drag of an individual particle, $6\pi \eta a$. The quantity $\dot{H}$ is the Hessian of $U$ in the $x_{eq}$ configuration scaled on the characteristic bond stiffness, $k_0$. This network model represents the gel as harmonic springs connecting bonded particles in the configuration $x_{eq}$. The perturbation may be decomposed into normal modes, $v_i$, $i = 1, 2, \ldots, 3N$, with respective scalar weights $C_i$, for which: $\delta(t) = \sum_{i=1}^{3N} C_i v_i e^{-\lambda_i t}$, and:

\[ \lambda_i \hat{R} v_i = \hat{H} v_i. \] (6.3)

Equation 6.3 describes the displacements of every particle in a normal mode and the corresponding relaxation rate, $\lambda_i$, of that same mode. The relaxation rates of the normal modes, are made dimensionless on the relaxation rate of a single particle pulled by a harmonic spring, $\lambda_0 = k_0 / (6\pi \eta a)$. The quantity, $\hat{R} = \dot{M}^{-1}$, is called the hydrodynamic resistance tensor, which is simply the inverse of the hydrodynamic mobility and maps the velocities of the suspended particles onto the set hydrodynamic forces resisting that motion.

These eigenvectors form a complete set of independent relaxation modes with structure given by particles in the positions $x_{eq}$ and interparticle interactions modeled as Hookean springs of stiffness $k_0$. The hydrodynamic resistance, $\hat{R}$, and $\hat{H}$, are the linear operators.
on which this generalized eigenvalue problem is posed. In the analysis of glassy and crystalline colloidal packings, many researchers have performed an analogous decomposition with harmonic springs between contacting particles [141, 142, 153], but with the additional approximation, $\mathbf{R} \to \mathbf{I}$ and the identity $\lambda_i = \omega_i^2$. Here $\mathbf{I}$ is the identity tensor and $\omega_i$ is thought of as a characteristic frequency of normal mode vibration in a mass-spring network having the same Hessian, $\hat{\mathbf{H}}$. The normal modes computed in this approximation are referred to as the normal modes of a "shadow" system behaving like an underdamped oscillator [154]. There are appealing analogies to molecular and atomic structures and their normal modes when analyzing this shadow system. However, at the colloidal scale the approximation $\mathbf{R} = \mathbf{I}$ is a severe one that neglects all hydrodynamic coupling between the particles. Additionally, colloidal dynamics are overdamped and the normal modes relax independently rather than vibrate as in the shadow system. As we will show, for colloidal gels, neglecting all hydrodynamic coupling leads to fundamentally different density of states for the relaxation rate $\lambda$ and different normal mode structures when compared with more realistic hydrodynamic models.

We address the role of different hydrodynamic forces by comparing the eigenvalues and eigenvectors generated by different controlled approximations for $\mathbf{R}$. Direct numerical simulations of the Stokes equations to find $\mathbf{R}$ exactly are challenging because such hydrodynamic resistance problems are ill-conditioned and solutions are computationally expensive to evaluate accurately [32]. However, approximations for $\mathbf{R}$ from multipole expansions and pair-wise additive modifications to account for hydrodynamic lubrication are readily computed [31]. Therefore, in determining a parsimonious hydrodynamic model it is of both great physical as well as computational value to understand how sensitive the normal modes in colloidal gels are to various hydrodynamic approximations. Chiefly, we are interested in how hydrodynamic lubrication arising largely from squeeze flows between pairs of nearly touching particles, so far neglected in our previous studies on the hydrodynamic of colloidal gelation (chapters 3 and 4), influences the normal modes. We also seek to understand how the normal modes with long-ranged hydrodynamic coupling differ from the freely draining approximation, which neglects all hydrodynamic interactions as in the shadow system. These two distinct physical effects: lubrication and long-ranged interactions, are addressed suc-
cessively by studying different hydrodynamic models for $\mathbf{R}$. The three models under study are: the Stokesian Dynamics model, which accurately represents both classes of hydrodynamic interaction, but has only been used to simulate up to $O(10^3)$ particles; the Rotne-Prager-Yamakawa model (RPY), which accounts for only long-ranged far-field hydrodynamic interactions, but can be extended to simulate up to $O(10^6)$ particles; and the freely draining model employed in conventional Brownian Dynamics (BD), in which all hydrodynamic interactions are neglected and the particles interact as in the shadow system.

6.3 Results

6.3.1 The role of hydrodynamic lubrication

The resistance tensor, $\mathbf{R}$ can be approximated quite accurately and efficiently for any particle configuration using the Accelerated Stokesian Dynamics (ASD) method [39,48]. ASD has been used to compute transport properties in suspensions of hard spheres with volume fractions up to random close packing and produces reasonable agreement with experimental measurements [49]. In this framework, $\mathbf{R}$ is a superposition of a far-field contribution due to long-ranged hydrodynamic interactions evaluated from a multipole expansion and a near-field component accounting for pair-wise lubrication forces: $\mathbf{R} = \mathbf{R}_{FF} + \mathbf{R}_{NF}$. The near-field component is dominated by squeezing flows between pairs of nearly touching particles generated by motion along their line of centers. As a consequence, the block of $\mathbf{R}_{NF}$ corresponding to interactions between bonded particles $i$ and $j$ is approximately proportional to the dyad $r_{ij}r_{ij}$, where $r_{ij}$ points between the centers of $i$ and $j$. For centro-symmetric interparticle interactions $U$ the block of the Hessian of $U$ corresponding to bonded particles $i$ and $j$ is proportional to the same dyad.

Therefore, we postulate that for all particles in the gel, $\mathbf{R}_{NF}$ is approximately congruent to the Hessian of the interaction potential [32]. If this postulate holds, we can make the following simplifying assumption: $\mathbf{R}_{NF} \approx \mu \mathbf{H}$, such that $\mathbf{R} = \mathbf{R}_{FF} + \mu \mathbf{H}$. The parameter $\mu$ can be understood as the relaxation time for a spring connecting nearly touching particles, whose relaxation is modulated by the squeeze flow between the particles. The hydrodynamic
drag in that scenario scales as the inverse of $\xi$, where $\xi = r_{eq} - 2a$ is the equilibrium separation between neighboring particle surfaces. When the time scale $\mu$ is made dimensionless on $6\pi \eta_0 a/k_0$, it can be written in the simple form: $\mu = a/\xi$. Particles that are closer together relax more slowly in response to the spring due to the squeeze flow between their surfaces.

Substituting the postulated form: $\hat{\mathbf{R}} = \hat{\mathbf{R}}_{FF} + \mu \hat{\mathbf{H}}$, into equation (6.3) yields a new eigenvalue problem:

$$\lambda_{FF,i} \hat{\mathbf{R}}_{FF} \mathbf{v}_i = \hat{\mathbf{H}} \mathbf{v}_i,$$

having the same eigenvectors as (6.3) and new eigenvalues that are related to the eigenvalues of (6.3) by:

$$\lambda_i = \frac{\lambda_{FF,i}}{1 + \mu \lambda_{FF,i}}.$$  (6.5)

(6.4) is a generalized eigenvalue problem whose solution are normal modes for a harmonic network with an approximation of the hydrodynamic resistance given by $\hat{\mathbf{R}} = \hat{\mathbf{R}}_{FF}$. That is, (6.4) describes the normal modes when only far-field hydrodynamic coupling among the particles is considered. Therefore, if the postulated congruence of the near-field hydrodynamic interactions and the Hessian holds, the effect of hydrodynamic lubrication is simply to reduce the relaxation rates of the true normal modes, $\lambda_i$ relative to $\lambda_{FF,i}$. Additionally, hydrodynamic lubrication does not change the spatial structure of the modes, as the same $\mathbf{v}_i$ appear in both (6.3) and (6.4). The characteristic time scale $\mu$ relates the relaxation spectrum of models for $\hat{\mathbf{R}}$ neglecting hydrodynamic lubrication, $\hat{\mathbf{R}} \approx \hat{\mathbf{R}}_{FF}$, to those including it, $\hat{\mathbf{R}} = \hat{\mathbf{R}}_{FF} + \hat{\mathbf{R}}_{NF}$.

To determine if the normal modes from (6.3) and (6.4) are in fact related as postulated, we compare the normal modes from different hydrodynamic models. We consider gels formed from 500 particles and compute $\hat{\mathbf{R}}$ using ASD and $\hat{\mathbf{R}}_{FF}$ using the inverse of the Rotne-Prager-Yamakawa (RPY) mobility tensor, which treats the particles as renormalized Stokeslets. First, the normal modes of (6.4), the eigen-pairs $\{\lambda_{FF,i}, \mathbf{v}_{FF,i}\}$, are calculated. Then the value $\mu_i$ that best satisfies (6.3) using the eigen-pair: $\{\lambda_{FF,i}/(1 + \mu_i \lambda_{FF,i}), \mathbf{v}_{FF,i}\}$ is determined by minimizing the objective function:

$$f(\mu_i) = \| \frac{\lambda_{FF,i}}{1 + \mu_i \lambda_{FF,i}} \hat{\mathbf{R}} \mathbf{v}_{FF,i} - \hat{\mathbf{H}} \mathbf{v}_{FF,i} \|_2.$$  (6.6)
Figure 6-2: Top: $\mu$ computed by minimizing $f(\mu_i)$ with $N = 500$ is independent of $\lambda_{FF,i}$. Bottom: The corresponding approximation error as a function of $\lambda_{FF,i}$. It is negligible for $\lambda_{FF,i} < 1$.

$f(\mu_i)$ is the norm of the difference between the left and right hand sides of (6.3) after substituting $\lambda_i = \lambda_{FF,i}/(1 + \mu_i \lambda_{FF,i})$ and $v_i = v_{FF,i}$. When the objective function is minimized, a normal mode of the far-field problem, $v_{FF,i}$ with associated relaxation rate $\lambda_{FF,i}/(1 + \mu_i \lambda_{FF,i})$, best represents a normal mode of the full hydrodynamic problem. For each normal mode, a different value of $\mu_i$ might minimize $f(\mu_i)$. The postulate formed by replacing $R_{NF}$ with $\mu H$ asserted that a single time constant $\mu$ could be used to remap all the eigenvalues between problems. For consistency with the postulate, we expect to find nearly constant optimal values for $\mu_i$ across different modes.

We plot the optimal value of $\mu_i$ as a function of $\lambda_{FF,i}$ in figure 6-2 and also depict $f(\mu_i)/||\hat{H}v_{FF,i}||_2$, which is a measure of the normalized error of this approximation for each mode. The optimal value of $\mu_i$ is nearly independent of $\lambda_{FF,i}$ at a fixed volume fraction. That is, for a given particle volume fraction, the same time constant $\mu_i = \mu$ can be employed to make nearly any normal mode of the far-field problem consistent with the full hydrodynamic one. As $\phi$ increases, so does $\mu$, which may be interpreted as the effective equilibrium separation between particles, $\xi$, decreasing slightly at higher volume fractions. Direct computation of the average surface to surface separation between bonded particles yields values matching with $a/\mu$ at each volume fraction, as would be expected. The time constant $\mu$ inferred this
way represents a sort of speed limit on the relaxation processes within the gels. From (6.5), when \( \lambda_{FF,i} \gg \mu^{-1} \), we find \( \lambda_t \approx \mu^{-1} \), such that no modes of the full hydrodynamic problem relax faster than the rate \( \mu^{-1} \).

These results suggest that for virtually all the modes computed the approximation \( \hat{\mathbf{R}}_{NF} = \mu \hat{\mathbf{H}} \) holds. A normal mode analysis employing the RPY model enables prediction of the normal modes of the full hydrodynamic problem. This can be understood by recognizing that slowly relaxing normal modes involve collective motion of the particle network and are unaffected by the localized squeezing flows accounted for in the near-field part of the hydrodynamic resistance tensor. The far-field model alone is able to capture the structure and relaxation rate of the slow modes quite accurately. The normalized error in approximating a full hydrodynamic normal mode with a far-field mode is smaller than 5% for modes with dimensionless relaxation rates, \( \lambda_{FF,i} \) smaller than 1. Larger normalized errors are found for modes with \( \lambda_{FF,i} > 1 \). As we will show, these fast modes involve localized rather than collective motion for which we might assume the details of the near contact hydrodynamic interactions to play a significant role. As a consequence, the eigenvectors in this part of the relaxation spectrum computed using the ASD and RPY models are expected to differ.

![Figure 6-3](image)

**Figure 6-3:** Top: \( \mu \) obtained by minimizing \( f(\mu_i) \) for systems with \( N = 100, 250, 500 \) and 1000 particles at \( \phi = 15\% \). Bottom: The corresponding approximation error as a function of \( \lambda_{FF,i} \). It shrinks drastically with increasing \( N \).

To examine the effect of system size on our approximation we compute \( \hat{\mathbf{R}} \) and \( \hat{\mathbf{R}}_{FF} \) for
$N = 100, 250, 500$ and $1000$ at a fixed volume fraction $\phi = 15\%$ and determine $\mu_i$ and the corresponding approximation error, as shown in figure 6-3. Both the proportion of fast modes and the error in $f(\mu_i)$ over the spectrum shrink with increasing $N$. The value of the best fit $\mu_i$ appears to grow systematically with the system size, $N$, but it is important to recognize that the structure of the gel also depends on $N$. For $\phi = 15\%$, the correlation length of the gel formed via arrested phase separation is on the order of 10 particle radii (see figure 6-1). Consequently, for the smallest system size in figure 6-3, the scale of the simulation box is on the order of the correlation length of the gel. Thus the gel structure and the nearest neighbor separation are changing with $N$ and would not be expected to give the same values of $\mu_i$ with different $N$. Instead, figure 6-3 simply indicates that the far-field approximation improves its ability to describe the normal modes of the full hydrodynamic problem with increasing system size, and that the effects of hydrodynamic lubrication influence only a small fraction of fast relaxation modes. Thus, the proposed renormalization may become exact in the limit $N \to \infty$. The values of $N$ that can be accessed with ASD simulations currently are limited. However, we have shown that the eigen-pairs $\{\lambda_{FF,i}, v_{FF,i}\}$ represent the relaxation spectrum of the full hydrodynamic problem well. Therefore, we switch now to understanding the collective modes of relaxation utilizing only the RPY mobility as a far-field approximation for the normal modes that can be extended to much larger system sizes.

### 6.3.2 The role of long-ranged hydrodynamic interactions

To understand how long-ranged hydrodynamic coupling affects relaxation in colloidal gels, we make a comparison of normal modes obtained from the freely draining approximation used in Brownian Dynamics (BD), where $\hat{R} = I$ with those obtained from the RPY tensor using $10^4$ particles. We characterize the distribution of slow modes responsible for macroscopic viscoelasticity via calculation of the relaxational density of states. For both BD and RPY we solve (6.3) to determine the normal modes of the five different particle configurations for each value of $\phi$. This generates an extensive set of the relaxation rates and eigenvectors associated with the models at different volume fractions. At a given $\phi$, the set contains a total of 150,000 relaxation rates and eigenvectors from which we compute the DOS and
In figure 6-4 we plot the DOS obtained for each volume fraction with the BD and RPY models. The DOS as a function of relaxation rate, $P(\lambda)$, highlights the significant effect of long-ranged hydrodynamic interactions on the normal mode response in weak colloidal gels. For the BD model, we find an overabundance of slow modes. The DOS scales as $\lambda^{-y}$, where $y \approx -1/2$ for $\phi = 15\%$. In contrast, for the RPY spectrum, the occurrence of slow and fast relaxation modes is equally probable, and $y = 0$ for all $\phi$. Long-ranged hydrodynamic interactions through the suspending medium enhance collective large-scale relaxation dynamics and consequently the fraction of fast modes increases relative to slow modes when compared to the BD approximation. With increasing $\phi$, differences between the two hydrodynamic models diminish and $y$ approaches zero as the fraction of slow modes decreases for the BD model. These different DOS are analogous to observations from polymer physics. A dilute solution of ideal polymer chains obeying the Zimm model, which treats the hydrodynamic interactions in the same way as the RPY model, has $P(\lambda) \sim \lambda^{-1/3}$. In contrast, when hydrodynamic coupling is neglected as in the Rouse model (equivalent to BD), $P(\lambda) \sim \lambda^{-1/2}$ [46]. Long-ranged hydrodynamic interactions tend to flatten the distribution of relaxation rates as collective motion through fluid mechanical coupling accelerates stress.
relaxation in soft materials.

It is important to note that there is no way of knowing in advance how the distribution of relaxation rates should scale without performing a normal mode analysis. In the case of dilute polymer solutions, exact solution of the normal modes in the Zimm model is not possible and a pre-averaging approximation is applied to the Oseen tensor to yield the analytical result $P(\lambda) \sim \lambda^{-1/3}$. This approximation has been tested via direct calculation of the normal modes and confirmed by experiment [46]. In much that same spirit, we have used a normal mode analysis of colloidal gels for increasing particle concentrations in the harmonic network limit to understand the role of different hydrodynamic interactions in determining the distribution of relaxation rates. We find distinct roles for lubrication and long-ranged hydrodynamic interactions and significant departures from the freely draining approximation with this direct numerical simulation of the relaxation spectrum for the harmonic network model. Neglected from this analysis are relaxation modes due to excluded volume interactions and the breakage and reformation of colloidal bonds. Both may play an additional role in the relaxation spectrum, and comparison of experiments with this baseline calculation should be used to validate the calculation.

The DOS computed from the eigenvalue problem is intimately related to stress relaxation in the gels. To confirm that the solutions to (6.3) were computed accurately, we perform dynamic simulations of the stress relaxation in colloidal gels following a step-strain deformation. The interactions among the particles in the gel configurations are modeled precisely as in the harmonic network model. Each pair of bonded colloids is connected with a permanent Hookean spring having rest length $2a$, and nonbonded particles interact only hydrodynamically. The gels are subjected to a shear step-strain of 1% during which all particles undergo affine motion. Then, the particles are allowed to relax back to equilibrium. The virial contribution to shear stress is computed as a function of time, and an ensemble average of this quantity is used compute the relaxation modulus, $G(t)$.

The relaxation modulus is proportional to the Laplace transform of the DOS:

$$G(t) - G_\infty \sim \int_0^\infty P(\lambda) \exp(-t\lambda) d\lambda,$$

(6.7)
where $G_\infty$ denotes the infinite time value of the modulus, a purely structural or thermodynamic quantity [104]. In the case of a DOS with power law scaling $\lambda^{-y}$ at small values of $\lambda$, (6.7) yields $G(t) - G_\infty \sim t^{-(1-y)}$, in the long time limit. Figure 6-5 plots the relaxation modulus for the step-strain simulations. The power law decay at all volume fractions for the RPY model is $G(t) - G_\infty \sim t^{-1}$. In contrast, the decay of the relaxation modulus with time steepens with increasing volume fraction in the BD model. At low volume fractions, the BD simulations give $G(t) - G_\infty \sim t^{-1/2}$, while at higher volume fractions the power law exponent approaches $-1$. Therefore, the computed DOS in figure 6-4 and values found for $\gamma$ are consistent with the results of dynamic simulations employing the same hydrodynamic and harmonic network approximations for the colloidal gels.

To characterize the structure of the normal modes we compute the collectivity index [135],

$$\kappa_i = \frac{1}{N} \exp \left( -\sum_{j=1}^{N} \nu_i |\mathbf{v}_i^{(j)}|^2 \log \left( \nu_i |\mathbf{v}_i^{(j)}|^2 \right) \right), \quad (6.8)$$

where $\nu_i$ is the normalization constant: $\nu_i^{-1} = \sum_j |\mathbf{v}_i^{(j)}|^2$, and $\mathbf{v}_i^{(j)}$ is a vector associated with particle $j$ reflecting its contribution to the normal mode $i$. The collectivity index measures
the extent to which particles participate in each mode. A mode that excites a larger number of particles in the gel has a higher collectivity index. With increasing volume fraction the degree of participation increases due to increased rigidity of the gel. In figure 6-6, we plot the likelihood of observing a mode with collectivity index $\kappa_i$ for all gels and both hydrodynamic models under study.

We find that the normal modes are more likely to have higher collectivity in the RPY model. Long-ranged hydrodynamic interactions lead to coupling and excitation of a larger fraction of the particles. As the volume fraction increases, differences between the two hydrodynamic models diminish. For $\phi = 45\%$, crowding leads to hydrodynamic screening, and $P(\kappa_i)$ is similar for both the BD and RPY models. The small $\kappa_i$ tail of the distributions corresponds to fast modes, $\lambda_i > 1$, for which relaxation is faster than the bare particle rate $\lambda_0$, and the normal modes are localized to only a few particles. The probability density of $\kappa_i$ is similar for both models in these tail regions.

Figure 6-6: The probability density for the collectivity index of all gels, modes and both models under study shows that the normal modes are more likely to have a higher participation in the RPY model.
6.3.3 The role of higher order hydrodynamic moments

In using the RPY approximation for long-ranged hydrodynamic interactions, higher order moments in the hydrodynamic scattering series were neglected [32]. However, the hydrodynamic torque, stresslet, and higher order traction moments in the colloidal gel also may also affect the relaxation dynamics. As discussed previously, the algorithm used to rapidly compute RPY interactions also allows for explicit accounting of higher order multipoles of the hydrodynamic traction on the particle surfaces [37]. Figure 6-7 compares the density of states obtained from the RPY model with a hydrodynamic model that accounts for next higher order multipoles: the torque and stresslet, which is denoted the Force-Torque-Stresslet, or FTS model. Here, the mobility used in the normal mode analysis is \( \hat{M} = \hat{M}_{UF} - \hat{M}_{US} \hat{M}_{ES}^{-1} \hat{M}_{EF} \), where the individual mobilities are blocks of the grand hydrodynamic mobility matrix and linearly couple force to velocity(UF), stresslet to velocity(US), stresslet to strain(ES) and force to strain(EF) on particles, respectively [48]. The DOS at each \( \phi \) match very well those computed via the RPY model, indicating that the relaxation rate and collective dynamics of the gel are largely unaffected by higher order moments of the traction.

![Figure 6-7: The density of states as a function of relaxation rate, \( P(\lambda) \), computed using the RPY model is compared to the FTS model, which includes higher order hydrodynamic traction moments. The results indicate that the collective relaxation dynamics are not qualitatively affected by the higher moments of the force density.](image)

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6.3.4 The dispersion relation for relaxation modes

We compute the correlation length of each normal mode through a quantity used in the analysis of flow structures in turbulent flow, the Karhunen-Loève decomposition: [155]:

\[
S_{v_i}(q) = \lambda_i \nu_i \sum_{j,k=1}^{N} v_i^{(j)} \cdot v_i^{(k)} \exp \left( i q \cdot (x_{eq}^{(k)} - x_{eq}^{(j)}) \right),
\]

(6.9)

with \(x_{eq}^{(j)}\) the position of particle \(j\) in the \(x_{eq}\) configuration. For a normal mode \(i\), the set of \(v_i^{(j)}\) forms a field:

\[
v_i(x) = \sum_j v_i^{(j)} \delta(x - x_{eq}^{(j)}).
\]

(6.10)

The Karhunen-Loève decomposition is proportional to the Fourier transformation of the autocorrelation of that vector field, such that \(S_{v_i}(q) \sim \mathbf{v_i}(q) \cdot \mathbf{v_i}(-q)\), where:

\[
\mathbf{v_i}(q) = \mathcal{F}(v_i(x)) = \sum_j v_i^{(j)} \exp(i q \cdot x_{eq}^{(j)}),
\]

(6.11)

\(S_{v_i}(q)\) is analogous to the static structure factor of the gel and characterizes spatial organization of a normal mode \(i\). However, unlike the static structure factor, the correlation is weighted by the amount that each particle participates collectively in the normal mode through the dot product \(v_i^{(j)} \cdot v_i^{(k)}\). A peak in \(S_{v_i}(q)\) reflects the spatial correlation length of the normal mode just as a peak in the static structure factor reflects the spatial correlation length of the underlying gel structure. The association between the correlation length of normal modes and their relaxation rate forms a dispersion relation for the gel that describes how quickly modes spanning a certain length scale relax in response to a perturbation.

Each of the 150,000 modes calculated for the gels at \(\phi = 15\%, 30\%, \text{ and } 45\%\) possesses different \(\lambda_i\) and \(S_{v_i}(q)\) with peak at \(|q| = q_i\). The relaxation rates and peak wavevectors from individually sampled normal modes form a continuous, multivariate distribution \(P(\lambda, q)\), extending the density of states \(P(\lambda)\). A scatter plot (not shown) of the sampled relaxation rates and wavevectors indicates that the dispersion relation follows a power law. To quantify the dispersion relation in an ensemble averaged sense, we construct a sample mean of \(S_{v_i}(q)\) over sets of modes having relaxation rates \(\lambda_i\) that fall within finite logarithmically spaced,
finite width bins. The set of computed normal modes possesses enough samples that all the bins contain at least 10 modes. For the modes within a bin of width $\Delta \lambda$, an average:

$$S_{\lambda}(q) = \frac{\sum_{i \in S} S_{\lambda i}(q)}{\sum_{i \in S} 1}, \quad (6.12)$$

with $S = \{ i : |\lambda_i - \lambda| \leq \Delta \lambda \}$ is computed. The peak in $S_{\lambda}(q)$ for each bin as well as the peaks associated with each individual sample within that bin are identified. The average relaxation rate in a bin, $\lambda$, and the peak wavevector of the corresponding $S_{\lambda, i}(q)$, denoted $q$, are the pair of coordinates describing the dispersion relations of the gels.

Figure 6-8: The average relaxation rate in a bin, $\lambda$ as a function of the peak wavevector $q$ of the corresponding $S_{\lambda, i}(q)$, displays qualitatively different power law scalings for the BD and RPY models.

Figure 6-8 plots $\lambda$ versus $q$ for all the gels using both the BD and RPY models. We observe a power law trend: $\lambda \sim q^\ell$, that depends qualitatively on the hydrodynamic model. For the RPY model, $\ell \approx 2$ and the scaling of relaxation rate with spatial correlation length.
is independent of $\phi$, much the same as with the density of states. In contrast, the BD modes exhibit significant dependence on volume fraction. For $\phi = 15\%$, we find $\ell \approx 3$, while at higher volume fractions $\ell$ decreases. The dispersion relation for the BD model approaches that of the RPY model. These results indicate that normal modes correlated over a length scale $l \sim q^{-1}$ always relax faster in the RPY model than in the BD model. The effect of the suspending solvent on normal mode structure of these amorphous colloidal systems is substantial and suggests that fluctuations are excited across larger length scales because of the long-ranged hydrodynamic interactions among the particles.

![Figure 6-9: Left: The variation $r_i$ around the peak wavector $q$ for a sample of 1000 modes from the DOS for both hydrodynamic models and for all three volume fractions studied. Right: The distributions $P(r)$ of the same residuals are normally distributed with mean 0.](image)

Care must be taken to ensure that the peak wavevector determined from the ensemble average is representative of the underlying samples. The variation of the sampled wavevectors about the ensemble averaged value is characterized by computing: $r_i = (q_i - q)/q$, for each mode $i$. This is the relative variation in the peak wavevector of each of the modes with respect...
to the value determined from the ensemble average. Figure 6-9 plots $r_i$ as a function of $q$ for $10^3$ samples at each volume fraction as well as a histogram of these normalized residuals. The residuals are normally distributed about the ensemble averaged value suggesting that the underlying distribution of the sampled $\lambda_i$ and $q_i$ can be modeled as:

$$P(\lambda, q) \sim \exp \left( -\frac{(q/q_{\text{model}}(\lambda) - 1)^2}{s^2} \right) P(\lambda),$$

(6.13)

with $q_{\text{model}}(\lambda) = c\lambda^{1/\ell}$ reflecting the inferred dispersion relation.

The relaxation rate can be thought of as the ratio of an effective elastic bond strength, $k(l)$, and an effective viscous drag coefficient, $\zeta(l)$, such that: $\lambda \sim k(l)/\zeta(l)$ [145]. The dispersion relation arises due to the variations with respect to $l$ of the elasticity and drag coefficient, characteristic of the relaxation of a normal mode having correlation length $l$. The elastic response of a domain of size $l$ is characterized by a spring constant $k(l) \sim l^{-z}$, which is size dependent due to the tenuous nature of the bonds within the domain. With increasing $l$, a smaller fraction of bonds connect the domain to the rest of the gel, which leads to softening and a decrease in $k(l)$. $z$ is the elasticity exponent and is sensitive to the nature of the bonds and the resulting stiffness of the gel backbone [156]. In our study we consider only central forces between the particles, which leads to no bending rigidity and an exponent $z < 3$ that will depend solely on the backbone structure at given $\phi$ [157, 158]. The viscous drag $\zeta(l)$ experienced by the domain will depend on the hydrodynamic model chosen. We therefore expect differences between the dispersion relations for the two models. For the BD model, we have seen that the drag on a domain of size $l$ relaxing in a viscous medium scales as $l^{d_f}$ so that $\lambda_{BD} \sim l^{-(d_f+z)}$, where $d_f$ is the fractal or Minkowski-Bouligand dimension of the gel [79]. For the RPY model, the drag is linear in $l$ such that $\lambda_{RPY} \sim l^{-(1+z)}$. We cannot know the elasticity exponent of the gels a priori, however from the observed dispersion relation of the RPY spectrum, $\lambda \sim l^{-2}$, we conclude that the elasticity exponent $z$ of the $\phi = 15\%$ gels under study is approximately 1. Employing the box counting method we determine that $d_f$ of the gels at $\phi = 15\%$ is 2.1, so that $d_f + z \approx 3.1$, which yields the observed scaling exponent for the BD dispersion relation. Therefore, the dispersion relations of the BD and RPY models for 15% particles by volume are consistent with an elasticity exponent of $z \approx 1$. 

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As $\phi$ increases, hydrodynamic screening makes the effective drag coefficients for the two models similar, and $\zeta(l)$ on the domains scales as roughly $l^{-2}$. Additionally, the fraction of isostatic particles, those with six or more bonded neighbors, increases to more than 92% for $\phi = 45\%$. Consequently, the elasticity exponent, $z$ approaches 0 because the number of dangling chains in the gel, which lead to softening over larger length scales, is greatly diminished in the rigidified microstructure. Therefore, the dispersion relations for both models at the highest volume fraction are similar: $\lambda \sim l^{-2}$. Unexpectedly, while both the elasticity exponent and the drag coefficient for the normal modes are expected to change with volume fraction, the power law scaling of the dispersion relation for the RPY model remains the same regardless of particle packing fraction. For now we cannot explain how $k(l)$ and $\zeta(l)$ change independently with volume fraction in the RPY model, yet they produce virtually the same dispersion relation at each concentration studied.

6.4 Implications for the rheology of weak colloidal gels

We have detailed the influence of hydrodynamic coupling on the relaxation dynamics of a colloidal gel in the linear response limit via normal mode analysis. However, these calculations rely on a key approximation: the conservative interparticle forces are treated as simple Hookean springs. This approximation enabled analytical progress, but is not necessarily consistent with real colloidal interactions. Here, we compare data from dynamic simulations employing hard sphere and depletion interactions [112] and experimental results in which the same interaction potential has been measured [159].

Recall, that the relaxation modulus is proportional to the Laplace transform of the DOS. Step-strain simulations with the Hookean spring approximation were already used to validate the DOS calculations. However, the conclusions drawn from the computed DOS may not translate to stress relaxation in materials without idealized interaction potentials. In the harmonic network, nonbonded particles do not interact directly following a step-strain. However, nonbonded hard spheres in a depletion gel will produce additional excluded volume interactions not reflected in the harmonic network. At the very least, the DOS and analysis of the structure of the normal modes suggest that the relaxation modulus at long times
should decay significantly faster in simulations employing the RPY model when compared to simulations using the BD model. In figure 6-10 we plot the previously published step-strain response for an experimentally studied depletion gel [159] and the calculated relaxation modulus, $G(t)$, from dynamic simulations using both the BD and RPY models. The simulated gels experience the same interaction potential used to generate the gel structures studied in the normal mode analysis.

![Graph of relaxation modulus $G(t)$](image)

**Figure 6-10:** The relaxation modulus $G(t)$ in response to a step-strain is strongly affected by the choice of hydrodynamic model in dynamic simulations employing hard sphere and depletion interactions. Measurements were averaged over 500 realizations for each data set to reduce thermal noise. Also shown (violet stars) are results from an instantaneous stress relaxation experiment of a colloidal gel with $\phi = 20\%$ [159].
At short times, the stress decay in the simulations reflects fast relaxation modes due to the hard core repulsion of the particles [41, 89]. These decay modes are absent in the DOS computed from the harmonic network approximation. For longer lag times hydrodynamic interactions influence stress relaxation and there are clear differences between the hydrodynamic models employed. For $\phi = 15\%$, the BD model gives $G(t)$ with a power law scaling $t^{-1/2}$, while the RPY model exhibits significantly faster relaxation, as $t^{-1}$. For both hydrodynamic models, $G(t)$ displays the asymptotic scaling predicted by (6.7) using the DOS of the harmonic networks. Additionally, the scaling of the RPY model at long times is in excellent agreement with the measured relaxation modulus in the experiment demonstrating that long-ranged hydrodynamic interactions play an essential role in macroscopic stress relaxation of gels. At short lag times however, simulation and experimental results diverge. This is expected because the step-strain simulations neglect hydrodynamic lubrication, which alters the relaxation of localized, fast modes.

For $\phi = 30\%$, the stress relaxation of the RPY model at long times appears to match the predictions of the DOS analysis. However, the BD model does not exhibit the faster stress relaxation anticipated from the DOS. For $\phi = 45\%$, both the BD and RPY models deviate from the DOS predictions at long times. These persistent differences may stem from the relaxation of deformed local packings via the hard core excluded volume interactions. We find that at high volume fractions, these entropic interactions are the biggest part of the virial contribution to the shear stress. It makes some sense that the performance of the harmonic network model would become worse with increasing particle volume fraction since excluded volume interactions are explicitly neglected and are not reflected directly in the DOS computed. We had expected that at long times the predictions of stress relaxation from the DOS would ultimately emerge. However, carrying out longer lag time simulations and still compute an ensemble average of the shear stress accurately in simulations with more $\mathcal{O}(10^4)$ particles is currently computationally prohibitive. Resolving this discrepancy in the decay of $G(t)$ at high volume fractions and long lag times is left for future work.

Overall, at low volume fractions, where caging is not a dominant physical mode, the DOS computed from the harmonic network approximation with the RPY hydrodynamic model accurately describes stress relaxation in a gel built from hard spheres and driven
to aggregate by a depletion attraction. At high volume fractions, the harmonic network approximation fails. However, softer repulsive interactions between nearly touching colloids will result in an interparticle potential whose mechanical equilibrium is better represented by a Hookean spring. Such interactions are easily engineered through use of polymer brush layers or surfactants attached to the surface of suspended particles to act as steric stabilization against van der Waals attractions or particle sintering. The DOS derived from the harmonic network approximation may yield even better predictions of the rheology of such materials.

6.5 Conclusion

We have computed the normal modes of weak colloidal gels with different approximations for the hydrodynamic interactions between the constituent particles. Our results show that the dynamics of a gel are a sensitive function of the hydrodynamic model. Long-ranged hydrodynamic interactions enhance the rate of stress relaxation in a strained gel and play a crucial role in determining the macroscopic properties of weak colloidal gels. As suggested in earlier chapters, hydrodynamic lubrication merely modulates fast, localized relaxation modes. With increasing volume fraction, hydrodynamic screening occurs, the majority of particles are multiply bonded, and the gel dynamics are less sensitive to the hydrodynamic model. We have confirmed the normal mode predictions at low and moderate particle concentrations by performing stress relaxation simulations of the same gels. We also successfully compared our results to experimental observations without the harmonic network approximation. A computational model neglecting hydrodynamic interactions will yield erroneous estimates of $G(t)$ or the complex modulus, among other related viscoelastic and mechanical properties in this concentration regime. Note that this analysis has neglected noncentral forces between bonded particles, which could affect the modes of relaxation and dynamics of strong gels.

The normal mode analysis conducted here examines the gel at one particular instant in time. Our methodology explicitly computes the relaxation time spectrum for hydrodynamically interacting colloids when supplied solely with a particle configuration and an estimate of the interparticle potential. In the case of athermal systems, such as granular media, foams and suspensions of large colloidal particles, recent advances in experimental techniques now
allow tracking of the real space dynamics of individual particles and reconstruction of overall particle configurations with limited resolution [142, 148, 154]. Ensembles of these gel structures can be analyzed and using our approach the DOS from each, along with those of nearby points in time can be computed and merged to yield a complete description of the relaxation spectrum. Such results could be utilized to understand the affect of aging and ripening as well as processing due to flow on both gel structure and viscoelasticity in a robust manner.

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Chapter 7

Large Scale Anisotropies in Sheared Colloidal Gels

7.1 Introduction

The percolated structure of colloidal gels imparts solid-like elasticity and other macroscopic material properties making them attractive for a wide range of specialized technologies. However, optimizing the final mechanical properties of gels requires careful control of the microstructural evolution of the colloidal dispersion. Breakdown of the network microstructure in colloidal gels subjected to external stresses is responsible for failure of these materials in applications essential to industry and of recent scientific interest [26]. For example, colloidal networks built from conductive carbon particles have been utilized as "flowable electrodes" in capacitive deionization processes for desalination [6,161] and in flow batteries for grid scale energy storage [162]. Flow of these networks through micro-fluidic electrode geometries can lead to breakdown of the network and formation of vorticity aligned flocs with significantly reduced electronic properties [163].

This instability of vorticity alignment is widely observed in a variety of dispersions of attractive particles: alumina and clay suspensions [164], attractive emulsions [165], carbon nanotubes [166], silica [167], polymer-colloid mixtures [168] and silica-filled PDMS liquids [169], among others. In the case of confined carbon black suspensions, even log-rolling structures aligned along the vorticity direction have been observed [170,171], the focus of the
next chapter. Scattering experiments on aggregated dispersions reveal a characteristic two-lobe "butterfly" pattern, with the long axis of the scattering pattern being oriented in the flow direction, indicating the emergence of an anisotropic microstructure as colloidal aggregates reconfigure during shear flow. In fact, similar butterfly scattering patterns, signaling vorticity aligned structure formation, are frequently observed in small angle light scattering (SALS) or small angle neutron scattering (SANS) experiments of various sheared complex fluids, including: semi-dilute polymer solutions [172, 173], worm-like micellar surfactants [174] and nanocomposites [175]. Recently, this anisotropy has been directly observed microscopically in 2D [176, 177] and 3D [178].

However, despite its ubiquity over the last 25 years, the origins of the vorticity alignment instability remain mysterious [26, 169, 179–182]. As has recently been shown by Colombo et al. using superposition rheology [183], microstructural anisotropy and selective structural breakdown also induces significant rheological anisotropy. To facilitate the engineering of a wide variety of novel soft materials utilizing anisotropic mechanical and optical properties, new constitutive models of the colloidal gel rheology are required that can describe and predict the amply observed flow induced restructuring.

Similar observations in phase-separating polymer systems have been explained by means of the Helfland-Fredrickson theory, where enhanced hoop stresses and polymer entanglement in the solution cause concentration fluctuations under shear and mixed flows [184, 185]. Here, fluctuations induce a first-order phase transition of an isotropic system to an anisotropic, phase separated state. This theory in conjunction with others suggesting the formation of stress-bearing structures [165, 175, 186], fails to explain the behavior observed in the flow-vorticity plane of colloidal dispersions and predicts elliptic scattering patterns instead of the two-lobe butterfly patterns. Alternatively, models describing ideal thixotropic materials and dealing with local anisotropy could be considered relevant. However, these models assume an inherent anisotropic microstructure mostly comprised of non-spherical elements. The constitutive equations track the breakdown of this anisotropic structure as a result of advection and the slow recovery to its initial state on cessation of flow [187]. A full explanation of the experimental observations of build up to global anisotropy during flow therefore awaits more complete understanding. What is required is the development of a
constitutive model able to describe instabilities in colloidal gels and how networks rearrange under shear.

While simulations of model colloidal particle dispersions provide the opportunity for deep mechanistic understanding of shear-induced ordering, the number of computational studies on aggregated colloidal dispersions under shear flow is limited. To date, no simulation has been able to reproduce the vorticity alignment effect or reported the observation of butterfly scattering patterns. It should be noted that certain computational models for flowing concentrated attractive spheres neglecting hydrodynamic interactions have shown that anisotropic particle organization could be obtained in these systems [188,189]. However, in this case the anisotropy was related to string formation of particles and the simulations predicted scattering results resembling Bragg-like peaks oriented in the vorticity direction, at odds with experimental observations. Log-rolling strings of particles normal to the plane of shear have been observed recently in experiments and simulations on confined dispersions [190], however the particles were non-attractive hard spheres and no large-scale features indicative of the butterfly scattering pattern were reported. In studies on the effect of flow on hard sphere dispersions, a series of Accelerated Stokesian Dynamics simulations showed that the incorporation of hydrodynamic interactions in computational models is crucial in order to recover the flow distorted microstructure seen in experiments [191]. Based on our findings from earlier chapters we expect hydrodynamic interactions to be equally important during the process of network breakdown.

In this chapter we study the steady shear behavior of colloidal gels composed of hydrodynamically interacting particles. The anisotropic microstructure resulting from the applied shear is presented in 7.3.1. It exhibits commonly observed scattering patterns reported in light, x-ray, and neutron scattering experiments. In section 7.3.2 we introduce a dimensionless parameter that ensures dynamic similarity of the steady state across a broad range of physical parameters – the strength of the shear flow relative to the most probable rupture force for the particle bonds. We study the effect of system size on shear and identify critical values of shear strength, below which system size and the role of confinement become relevant. We demonstrate that the non-hydrodynamic contribution to the relative viscosity of the dispersion, the degree of anisotropy and the characteristic size of the vorticity
aligned flocs can all be collapsed as a function of flow rate, particle volume fraction, and interaction strength using the same dimensionless parameter in sections 7.3.3–7.3.4. Finally, comparisons with simulations neglecting hydrodynamic flows are used in 7.4 to show that hydrodynamic interactions, which stabilize the vorticity aligned flocs under flow, are essential to describing these nonlinear flow instabilities.

7.2 Simulation details

In experiments, shear anisotropy is reportedly observed in correlations over length scales up to hundreds of particle radii [171,179,182]. In order to investigate these same length scales, simulations of colloidal dispersions with \( N = 216,000 \) spherical particles of mean radius \( a \) with \( d_a = 5\% \) polydispersity are conducted for volume fractions \( \phi = 5–30\% \). This allows us to resolve scattering in the range of \( 0.05 < qa < \pi \).

A short-ranged attraction is modeled with an Asakura-Oosawa form [43]. The width of the attraction is set at \( \delta = 0.1 \) and the depletion strength at contact, \( U_A \), is varied relative to the thermal energy of the particles, \( kT \). The parameter \( \epsilon = kT/U_A \) characterizes the strength of the interaction from the athermal, \( \epsilon = 0 \), to the hard sphere limit, \( \epsilon \to \infty \).

We employ simulations with the Rotne-Prager-Yamakawa tensor (RPY) to model the gelation of the attractive dispersion in a solvent of viscosity \( \eta_s \) for \( 10^3 \) bare diffusion steps \( \tau_D = 6\pi\eta_s a^3/kT \) at which point all samples are found to be percolated. Each gel is then exposed to steady shear for \( \gamma = 500 \) strain units enforcing Lees-Edwards boundary conditions [61]. The strength of shear is varied by adjusting the strain rate \( \dot{\gamma} \), thereby tuning the Mason number, \( Mn = 6\pi\eta_s a^2\delta\dot{\gamma}/U_A \), a measure of the shear force exerted on a particle relative to the bond force of the particle pair at contact. The system under steady shear deformation is studied for values of: \( Mn = 10^{-3} - 10^1 \) and \( \epsilon = 0 – 0.2 \), while the 2D scattering patterns of the microstructure and the evolution of the number of particles, \( N_g \), in and characteristic length, \( L_g \), of the aggregates are measured. The degree of anisotropy along with characteristic length scales of fluctuations in the sheared dispersions are quantified, and we compute the virial contribution to the relative shear viscosity, \( \eta_r = (\eta - \eta_\infty)/\eta_s \). Here, \( \eta \) and \( \eta_\infty \) are the total and the purely hydrodynamic contribution to the dispersion viscosity, respectively. All
results are averaged over three independently generated samples for each combination of $\phi, \epsilon$ and Mn.

### 7.3 Results

#### 7.3.1 Measurements of shear anisotropy

2D scattering patterns of the micro-structure of the system under steady shear deformations with increasing Mason numbers for several attraction strengths in the flow-gradient (1–2) (figure 7-1) and flow-vorticity (1–3) planes (figure 7-2) are shown for $\phi = 20\%$. The local microstructure in the 1–2 plane, for both low $\epsilon$ at high Mn and high $\epsilon$ at all Mn (see figure 7-1), mirrors experimental SALS and SANS results that also identified an enhanced scattering along the extensional axis of the flow for sheared gels [168,182]. Similar observations were made for two-dimensional gels at interfaces [177,192]. The scattering lobes are parallel to the extensional axis, which clearly shows that, as for hard spheres, the microstructure is primarily oriented along the compression axis, expected from theory [132]. Here, correlations over large length scales manifest themselves through effective clusters formed along the compression axis.

However, at low $\epsilon$ and Mn, the scattering data deviates from the classic picture of shear alignment. Instead, the scattering lobes align with the velocity gradient. Visual observations of the microstructure show that the exerted shear stress does not break down the gel but instead leads to fracture and flow between periodic images of the percolated network. To understand this consider the breakup of an aggregate under shear. In simple shear flow, two domains of characteristic length scale $l$ become separated when the shear force exerted on them, the product of relative straining velocity $\dot{\gamma}l$ and hydrodynamic drag $\zeta$, exceeds the forces holding the domains together: $F$ [193,194]. In an unconfined dispersion then, for weaker applied shear larger aggregates will be present. In the case of simulations with a finite system size $L$ however, $l$ cannot exceed $L$, no matter how small $\dot{\gamma}l\zeta$ relative to $F$ becomes. The gel has to fracture in the shear plane due to the externally imposed steady shear. The response of the gel and the degree of breakup at a fixed Mn and $\epsilon$ is also dependent on its
Figure 7-1: Contour maps of 2D density fluctuations in the 1–2 plane at \( \gamma = 500 \) and \( \phi = 20\% \) for increasing Mn and all \( \epsilon \) under study show shear alignment along the compressional axis. The horizontal and vertical arrows indicate the flow and gradient directions, respectively. The size of the \( qa \)–domain shown is \([-1, 1] \times [-1, 1]\) and the color intensity scale on the right represents the absolute scattering values.

volume fraction \( \phi \). In section 7.3.3 we present a theory connecting the finite system size to this \( \phi \) dependence that has implications for experiments of gels in confinement.

In the 1–3 plane, the scattering patterns readily reveal a structural anisotropy characterized by the butterfly pattern. The anisotropic structure factors are a consequence of the colloidal network breaking down in a spatially selective manner with a loss of structure in the flow direction. The data are qualitatively and quantitatively comparable to earlier experimental measurements [195, 196]. The width of the lobes indicate density fluctuations in the flow direction on the order of 10–100 particle radii, in agreement with observations by Kim et al [182]. This is the first time that a discrete element simulation has been able to reproduce experimentally observed scattering patterns of sheared gels. Figure 7-2 also demonstrates that structural anisotropy increases with increasing shear, or Mn, as one would naively assume. However, if the magnitude of intensity in the butterfly pattern and the degree of spread of the two lobes are assumed to be indicative of the degree of anisotropy, the
correlation between shear and anisotropy is non-monotonic. Above a critical value of Mn, the butterfly patterns start to diminish in both intensity and size. This suggests that the transient structures that are created as a result of shear, can no longer resist the shearing force and the dispersion fully fluidizes, as also seen in confocal microscopy studies [159].

Next, the role of volume fraction on the response of sheared colloidal gels is investigated. Figure 7-3 shows the 2D scattering patterns in the 1–2 (a,b) and 1–3 (c,d) planes for increasing $\phi$ at $\epsilon = 0.1$ and Mn = 0.05(a,c) and Mn= 0.1(b,d). To facilitate the comparison the absolute scattering values $S$ are scaled by $\phi$ (Since the peak intensity scales as $S(q) \sim q^{-d_f}$ and $q \sim \phi^{1/d_f}$, $S \sim \phi^{-1}$ is expected in the low $q$ range [71]). In the 1–2 plane the degree of shear alignment increases with volume fraction at a fixed Mn. In the 1–3 plane the characteristic length scale, $q_{xx, max}$, where the maximum intensity is observed, increases with $\phi$. It is controlled by the degree of network breakdown at a given level of shear, as discussed in section 7.3.3.
Figure 7-3: Contour maps of 2D density fluctuations in the 1–2 [(a),(b)] and in the 1–3 [(c),(d)] planes at $\gamma = 500$ and $\epsilon = 0.1$ for all $\phi$ under study and $\text{Mn} = 0.05$ [(a),(c)] and $\text{Mn} = 0.1$ [(b),(d)] reveal that degree of shear alignment is strongly volume fraction dependent. The horizontal and vertical arrows indicate the flow and gradient directions [(a),(b)], and the flow and vorticity directions [(c),(d)], respectively. The size of the $qa$–domain shown is $[-1, 1] \times [-1, 1]$ and the color intensity scale on the right represents the absolute scattering values scaled by $\phi$.

Results for the 2D scattering patterns in the 1–2 (a,b) and 1–3 (c,d) planes, with the absolute scattering values $S$ scaled by $\phi$, of dispersions with $\phi = 10\%$ and $20\%$ at $\epsilon = 0.05$ for increasing $\text{Mn}$ are shown in figure 7-4. Scattering in the 1–2 plane again provides evidence of the system size effect for $\phi = 20\%$ at low $\text{Mn}$. In contrast, at $10\%$ the dispersion is shear aligned – at lower volume fractions network breakup is initiated at even smaller values of $\text{Mn}$. In the 1–3 plane the lobes of the butterfly pattern are consistently smaller and the scattering is stronger at the lower $\phi$. The length scale of density fluctuations along the flow direction is more clearly defined at smaller $\phi$ as network reorganization and breakup has progressed further at a given value of dimensionless strain rate.
Figure 7-4: Contour maps of 2D density fluctuations in the 1–2 [(a),(b)] and in the 1–3 [(c),(d)] lanes at $\gamma = 500$ and $\varepsilon = 0.05$ for increasing Mn and $\phi = 10\%$ [(a),(c)] and $\phi = 20\%$ [(b),(d)] show that Mn alone does not control the response of sheared colloidal dispersions. The horizontal and vertical arrows indicate the flow and gradient directions [(a),(b)], and the flow and vorticity directions [(c),(d)], respectively. The size of the $qa$–domain shown is $[-1, 1] \times [-1, 1]$ and the color intensity scale on the right represents the absolute scattering values scaled by $\phi$.

7.3.2 The characteristic rupture force $\bar{f}$

In the case of non-Brownian electrorheological fluids the Mason number, the ratio of hydrodynamic force to interparticle attraction, was found to be useful for collapsing rheological data taken at different strain rates and field strengths onto a single curve [197,198]. It was possible to describe the dispersion rheology using only Mn and $\phi$. In contrast, the sheared attractive dispersions studied here are Brownian and are best described in terms of Mn, $\varepsilon$ and $\phi$. The simulation results depend on both the strength of shear and scale of thermal fluctuations relative to the interparticle attraction. However, it is also possible to define a single force scale – the most probable rupture force for the intercolloid bonds, $\bar{f}$ – which accounts for the weakening of bonds due to thermal fluctuations. As will be shown, this force scale can be used to collapse data across a range of Mn and $\varepsilon$ in terms of a single dimensionless group.
In an attractive colloidal dispersion interparticle bonds have limited lifetimes due to thermal sampling of the energy barrier preventing un-bonding. When a bonded pair of particles is separated at a fixed rate, rupture of the bond is detected by a discontinuity in the applied force. Due to the stochastic nature of the particle trajectories, the process leads to a distribution of bond rupture forces with a most probable force exerted by the bond at rupture given by [199]:

\[ f \sim \frac{kT}{\delta} \log \left( \frac{\dot{f}\delta\tau_K}{kT} \right), \]  

(7.1)

Here, \( \tau_K \sim \frac{3\pi\eta_s a^2}{U_A} e^{1/\epsilon} \) is the Kramers escape time from a short-ranged attractive well of width \( \delta \) and depth \( U_A \), and \( \dot{f} \) is the rate at which the bond was loaded. Under shear, bonded particle pairs are subject to a tensile load at a constant loading rate set by \( \dot{\gamma} \), and the bond loading rate can be approximated as \( \dot{\gamma} a/\delta \left( U_A/\delta - \bar{f} \right) \). The quantity \( \dot{\gamma} a/\delta \) is the strain rate divided by the strain over which the bond ruptured, or equivalently the inverse of the characteristic time scale of the rupture event. Similarly, the quantity \( (U_A/\delta - \bar{f}) \) is the change in the force exerted by the bond over the rupture process. Therefore

\[ f \sim \frac{U_A}{\delta} + \frac{kT}{\delta} \log \left( \frac{(U_A/\delta - \bar{f})3\pi\eta_s a^2\delta^2}{kTU_A} \right). \]  

(7.2)

Solving for \( \bar{f} \) and rewriting in terms of \( M_n \) yields:

\[ \frac{\bar{f}\delta}{U_A} \sim 1 - \epsilon W \left( \frac{2}{M_n} \right), \]  

(7.3)

where \( W(s) \) is the Lambert function, the solution to \( W(s) = s \exp(-W(s)) \).

\( \bar{f} \) is smaller than the athermal bond rupture force, \( U_A/\delta \), due to the thermal activation of the bonds. The relevant strength of interaction for mapping structural and rheological properties is the force scale most likely to disrupt a bond on the time scale of the imposed shear, \( \dot{\gamma}^{-1} \). For instance, the effective bond strength is zero on time scales longer than the natural lifetime for spontaneous dissociation. On the other hand, if driven to unbind on time scales shorter than needed for diffusive relaxation, the strength of the bond will reach the athermal limit set by the maximum gradient in a potential of mean force. Note, \( \bar{f} \) becomes
negative when $\text{Mn} \leq 2\epsilon \epsilon^{-1/\epsilon}$. This limit is equivalent to $\dot{\gamma} \tau_K \leq 1$, in which a reverse flux can balance the forward flux for bond breakage. In this case, which is not relevant to the present study, an Eyring type rate expression should be used to map rheological properties rather than the most probable rupture force.

The shear forces made dimensionless on the most probable rupture force lead to a renormalized Mason number:

$$
\text{Mn}^* = \frac{6\pi \eta \alpha^2 \dot{\gamma}}{\bar{f}} = \text{Mn} \frac{U_A}{f \delta} = \text{Mn} \left(1 - \epsilon W \left(\frac{2}{\text{Mn}}\right)\right)^{-1}.
$$

(7.4)

In the small Mason number limit studied here, $\text{Mn}^* \approx \text{Mn}/(1 - \epsilon \log(2/\text{Mn}))$. Thus, $\text{Mn}^*$ is greater than $\text{Mn}$ by a logarithmic factor proportional to $\epsilon$. For modest values of $\epsilon$, this correction is significant, but it diminishes as $\epsilon$ approaches zero—the athermal limit.

### 7.3.3 Critical breakdown of network structure: system size effects

In simple shear flow, two aggregates of characteristic length scale $L_g$ become separated when the shear force exerted on them, $6\pi \eta \alpha L_g^2 \dot{\gamma}$, exceeds the forces holding the domains together. In the case of attractive colloids the relevant force is $\bar{f}$ and on the verge of breakup $6\pi \eta \alpha L_g^2 \dot{\gamma}/\bar{f} \sim O(1)$. Therefore the stable characteristic aggregate length scale is given by $L_g \sim \text{Mn}^*^{-1/2}$ [193, 194]. For a fractal aggregate of fractal dimension $d_f$, the number of particles in the aggregate scales as $N_g \sim L_g^{d_f} \sim \text{Mn}^*^{-d_f/2}$ so that at smaller strain rates larger aggregates are stabilized. For a percolated gel with $N$ particles in a simulation box of size $L$, $N_g \leq N$ and $L_g \leq L$. At a critical value of the renormalized Mason number, below which the system spanning percolated network is stable under shear flow, it is found that $N_g = N = N_c$, the critical aggregate size, and $L_g = L = L_c$, the critical length scale. Since $\phi \sim N/L^3$ this critical value can be estimated as:

$$
\text{Mn}^*_c = A \phi^{2/(3-d_f)},
$$

(7.5)

where the pre-factor is system size dependent, $A \sim N^{-d_f/2}$. Figure 7-5 plots the average size of the largest aggregate $N_g$ as a function of $\text{Mn}^*$ for all dispersions under study. In agreement
with the predictions, above a critical value, $\text{Mn}^*$ controls the stable aggregate size and $N_g \sim \text{Mn}^*^{-1.1}$. Applying the scaling theory leads to the conclusion that the aggregates have a structure characterized by $d_f^{\text{predicted}} \approx 2.2$. Additionally, it is indeed found that the onset of gel breakup, $\text{Mn}_c^*$, increases with volume fraction as $\text{Mn}_c^*(\phi) = 9.6\phi^{2.4}$, shown in the inset of figure 7-5. This finding is consistent with the scaling in equation (7.5) and suggests that the gels at the point of breakup have a fractal dimension $d_f^{\text{predicted}} = 2.15$. The predicted value of $d_f$ is validated by computing the box counting (Minkowski-Bouligand) dimension [79] for these dispersions with increasing $\text{Mn}^*$, independent from the measurements of $N_g$. For the dispersions studied we find at the point of breakup $d_f^{\text{measured}} = 2.15 \pm 0.10$, in excellent agreement with the prediction of the scaling theory.

Figure 7-5: The size of the largest aggregate present in the system $N_g$ at $\gamma = 500$ collapses remarkably well when plotted as a function of $\text{Mn}^*$ for all $\epsilon$ and $\phi$ studied for $N = 216,000$ (dashed line). For each volume fraction a critical $\text{Mn}_c^*$ can be identified, below which $N_g$ is controlled by the system size. $N_g$ is also measured for $N = 64,000$ (dotted line) at $\epsilon = 0.05$ and $\phi = 5\%$ (open symbols) and it is found that the breakup mechanism is solely controlled by $\text{Mn}^*$ and independent of system size. Inset: $\text{Mn}_c^*$ as a function of $\phi$ displays a power law scaling as expected from theory (line) and in agreement with measurements of $d_f$.

To confirm that the onset of breakup is indeed controlled by the system size, shear
simulations are also conducted for $N = 64,000$ particles at $\epsilon = 0.05$ and $\phi = 5\%$. $Mn^*_c$ increases with decreasing system size and the scaling pre-factor changes as predicted: $A(N = 64,000) = 34.4 \approx (64/216)^{-2/d_f} A(N = 216,000)$. Thus, given a balance of shear and rupture forces, for $Mn^* > Mn^*_c$ the value of $N_g$ is system size independent and is only controlled by the relative rate of shear $Mn^*$. This has great consequences for interpreting the response of dispersions under shear in simulations. For sufficiently low flow rates $N_g = N$ and the system spanning network will fracture along the shear plane as the gel flows past its periodic images intact. This is reflected in the 2D scattering patterns of the 1–2 plane shown in figure 7-1 for low $Mn$ and $\epsilon$ as discussed in section 7.3.1. Instead of the typical pattern for shear alignment along the extensional and compressional axes ($\theta = \pm 45^\circ$) for attractive dispersions, the scattering indicates overall alignment of the gel along the flow direction relative to its periodic images above and below. In order to draw system size independent conclusions, computational models need to operate above $Mn^*_c$, especially challenging for high volume fraction dispersions. Note that as $\phi \to \phi_{max}$, the maximum packing fraction, for dense suspensions $d_f \to d = 3$ and $Mn^*_c$ diverges. In the case of densely packed attractive glasses, the behavior under shear and the response to an external stress will be governed by geometric confinement as particles cannot move past each other due to crowding. In this particular case, however repulsion dominates the interaction as there is no space to fracture or form anisotropic structural elements.

7.3.4 Dynamic yield and steady shear response

Based on our observations and the presented 2D scattering patterns in figures 7-1–7-4, we expect the response of a sheared colloidal gel to fall into one of three possible regimes, as indicated in figure 7-6. For $Mn^* \ll Mn^*_c$, the stable aggregate length scale, $L_g$, of the gel exceeds the system’s confining dimension, $H$, along the velocity gradient direction and the gel is not sheared apart. Instead, the gel will undergo a dynamic yielding as bulk segments of gel slip past each other along a fracture plane. Rearrangement occurs when particle bonds are broken and new contacts are established, and can result in a time averaged net shearing motion that resembles the stop and hop motion of strongly bonded electrorheological fluids under shear [198]. For $Mn^* \gg Mn^*_c$ the aggregate length scale is solely controlled by the
strength of shear. As $Mn^*$ is increased, the aggregate size will continuously decrease until $L_g = a$, the primary particle size, and the gel is completely fluidized.

In the initial breakdown regime where $Mn^* \sim O(Mn^*_c)$ the stable aggregate size can be smaller than the confinement length, $L_g < H$. However, the number of aggregates $N_{ag} = N/N_g = (H/L_g)^{d_f}$ is very small. Typically, shear removes a number of small clusters from the gel network, but the majority of particles belong to a single aggregate and $N_{ag} \approx 1$. Reorganization of the network in the flow and vorticity directions is still possible. In this regime, experiments with a wide variety of materials observe the formation of "logs" which roll between the surfaces generating shear. It is challenging to think of such structuration within a rheometer as capable of producing a bulk measurement of rheological properties, because the microstructure is now a sensitive function of the geometry of the measurement device. The aggregate size relative to the confinement has to be small enough that the effects of confinement can be neglected. That is, $L_g/H < 1/C$, where $1/C$ is the fractional size of an aggregate compared to the constraining dimension, requiring a Mason number $Mn^* > Mn^*_cC^2$. For any particular dispersion and given value of $H$, the value $C$ needed to reach the bulk limit, and therefore the width of this intermediate regime, will depend on the detailed nature of the interparticle interactions and their interactions with the boundaries, however.

In the current simulations of spherical particles with an isotropic, short-ranged attraction, we observe responses characteristic of all three regimes. Scaled appropriately, all data for maximum cluster size falls on the single master curve that we present in figure 7-6. Note that observation of vorticity alignment and density fluctuations in the flow directions is not restricted to dispersions in the steady shear regime. In fact, we find butterfly patterns for a wide range of Mason numbers. This is a crucial point. Often in experiments, vorticity alignment as inferred from scattering data is interpreted as an indication of the breakdown of the system spanning microstructure. However, when computing the scattering intensities and simultaneously observing the microstructure, it is found that this not necessarily the case. Indeed, for large values of $Mn^*$, the gel is broken down into individual aggregates, which are aligned in the vorticity direction, as seen in experiments. However, as shown in the 2D scattering patterns, similar structural anisotropy in the 1–3 plane is also found at low values.
of Mn*. In this case, the gel remains percolating despite flowing and adopting an anisotropic microstructure. The flow still leads to preferential alignment of individual gel strands and a rearrangement of the network and pore structure resulting in shorter correlation lengths along the flow direction. As discussed in section 7.3.6 the anisotropic alignment factor and characteristic length scales are not dependent on the size or number of aggregates and so do not collapse with Mn*/Mn*, but solely depend on Mn*.

Figure 7-6: The stable aggregate length scale $L_g$ at a given shear strength Mn* reveals three different regimes of shear response of a colloidal gel under confinement: Dynamic yield, initial breakdown and steady shear. $L_g$ is measured relative to the length scale of confinement $H$ and the Mason number is scaled on the critical value for network breakdown, Mn*. The threshold $C = H/L_g$, required for statistically significant sampling of the bulk steady shear response, sets the width of the initial breakdown region. The legend is the same as in figure 7-5.

The confined shear response behavior discussed here is expected to be present for both simulations and experimental systems. In a computational model $H = L$, the size of the simulation box, whereas in a shear experiment $H$ is the physical gap size between plates that confine the fluid. Gelling silica particles under shear exhibit a critical strain rate below which plastic flow is observed before yielding [183]. For large strain rates, the loss of connectivity leads to structural breakdown along the flow direction and a gradual erosion of aggregate sizes.
with increasing $\dot{\gamma}$. As another example consider that available rheological measurements on carbon black dispersions show a clear transition from a fluidized regime to dynamic yielding as $\dot{\gamma}$ is reduced [200]. Analogous to $\text{Mn}^*$, the flow curves can all be collapsed using a critical strain rate marking the transition that is a function of both the interparticle attraction and the volume fraction [201]. Given an experimentally identified degree of confinement, our proposed interpretation of the flow curve might enable extraction of a characteristic aggregate size from rheological measurements.

Finally, experiments and simulations often probe the two extremes of the structural response, rarely overlapping. For simulations, the finite and small system sizes explored may make the necessary $\text{Mn}^*$ too large and steady shear response is not achievable. In experiments the required $\text{Mn}^*$ may be inaccessibly small, except for very confined dispersions, and the dynamic yielding regime may be difficult to observe. Nonetheless, because the response is solely dependent on $\text{Mn}^*$ it should be possible to observe all three behavior regimes in a single experiment using a cone-and-plate rheometer in which the degree of confinement varies with radial position, but $\text{Mn}^*$ is fixed. At the center the gap is small and sheared gel will span the entire gap, exhibiting dynamic yield. Moving radially outwards, the gap grows while the cluster size remains fixed. Eventually, the gel will find itself in the other two regimes, which might first appear in the form of log-rolling structures and then a more fluidized, opaque state as noted in recent experiments [167,170] and discussed in the next chapter. Given required flow rates and flow geometry in a particular engineering application, these scaling regimes can be used as constraints on the design to ensure percolation, structuration, or fluidization as desired.

### 7.3.5 Sheared gel rheology

These different structural responses are pertinent to the rheology of sheared colloidal gels. It has been observed previously that loss moduli during flow show a weak dependence on strain rate, and hence on the structural anisotropy. This suggests that the hydrodynamic contributions to the stress do not depend too strongly on the microstructure [183,202]. Therefore, here we consider the non-hydrodynamic relative viscosity $\eta_r$, which measures the contributions of hard sphere repulsions, and interparticle attractions to the stress –
sometimes called the virial contribution. In figure 7-7 $\eta_r$ is plotted in terms of $Mn^*$ scaled by $Mn_c^*$ for all dispersions under study. The data collapses onto a single master curve for $Mn^*/Mn_c^* < 1$, in the dynamic yield regime. Here, the viscosity decreases as $Mn^*^{-1/2}$ due to bond breakage and reformation along a fracture plane in the gel.

Figure 7-7: The steady-state virial contribution to the relative shear viscosity $\eta_r$ as a function of $Mn^*$ scaled by $Mn_c^*$ for all $\epsilon$ and $\phi$ studied collapses onto a single master curve for $Mn^*/Mn_c^* < 1$. Departure from the master curve for $Mn^*/Mn_c^* > 1$ is $\phi$ dependent. Also shown in the inset is this viscosity as a function of $Mn^*$ and the experimentally measured viscosity for adhesive hard spheres [196]. In the experiments, the viscosity is reported as a function of an inverse Bingham number which should be proportional to the Mason number. We shift this multiplicatively to align the structural data in the experiments and simulations based on figure 7-9.

For $Mn^*/Mn_c^* > 1$ the percolated gel network is broken down into smaller aggregates. The number of bonds broken will depend on the particle density and the departure from the master curve is therefore dependent on $\phi$. Eventually, $\eta_r \sim Mn^*^{-1}$ in the limit of large $Mn^*$ for all volume fractions. Under strong shear, the steady shear viscosity will be dominated by the hydrodynamic contribution which is not computed here. This contribution sets a high strain rate plateau viscosity, $\eta_\infty$, and may even contribute to mild shear thickening as the dispersion structure is degraded [170]. This behavior suggests that a dynamic yield stress
σY(ϕ) for Mn*/Mn* ≪1 should exist. However, in our simulations we impose a constant, finite strain rate through deformation of the boundaries so that the gel must always flow. This leads to stochastic fracture events between the gel network and its periodic images and consequently large observed stress fluctuations around the mean value of ηr, which we obtain by averaging over many independent samples. The stress in the simulation, σ, will always exceeds σY. To measure σY(ϕ) accurately it is necessary to implement carefully controlled fixed stress boundary conditions [203].

The inset of figure 7-7 depicts the virial contribution as a function of Mn* for all the cases under study as well as for experiments with octadecyl coated silica from Eberle et al [196]. These results show how the virial contribution to the viscosity grows with volume fraction at a given strain rate. Outside of the dynamic yield regime in which system size effects govern the energy dissipation mechanism, a similar scaling of the viscosity with Mason number is observed when compared with experiments. The quantitative comparison should not be overstated. In the experimental work, hydrodynamic forces on the particles were normalized by the experimentally measured yield stress of the gel to give a dimensionless parameter called the inverse Bingham number. It is shown that this can be related to the ratio of hydrodynamic forces to interparticle bond strength and thus is equivalent to a Mason number. However, the details of this estimation process matter for directly comparing the simulations with experiments, and no direct measurements of the interparticle forces were made.

7.3.6 Characteristic length scales of anisotropy

The alignment factor, A_f(q) is an order parameter that is typically used for scattering data acquired under an aligning field [204]. Computation of A_f(q) requires an integration of S(q = (qx, qy, qz)) weighted by spherical harmonics over all angles at a fixed wave length q = |q|. With θ the polar angle relative to the flow axis in the 1-3 plane, the typically computed order parameter is:

\[ A_f(q) = \frac{\int_0^{2\pi} S(q, \theta) \cos(2\theta) d\theta}{\int_0^{2\pi} S(q, \theta) d\theta}. \]
Computer simulations can only measure the structure factor on a finite Cartesian grid limiting the accuracy of such an angular integral. Instead, we choose to quantify the anisotropy in the sheared dispersions by directly comparing the one-dimensional scattering intensities along the flow, \( S(q_x, q_y = 0, q_z = 0) = S_x(q_x) \) and vorticity directions, \( S(q_x = 0, q_y = 0, q_z) = S_z(q_z) \), as done previously [196]. For each shear strength Mn* and attraction strength \( \epsilon \), a modified alignment factor is computed:

\[
\tilde{A}_f = \frac{\int_{q_{\text{min}}}^{q_{\text{zz}}} \langle S_x \rangle - \langle S_z \rangle \, dq}{\int_{q_{\text{min}}}^{q_{\text{zz}}} \langle S_x \rangle + \langle S_z \rangle \, dq}.
\]

Here, the angle brackets indicate an average over 50 steady-state strain cycles starting at \( \gamma = 450 \) and the integral is computed from the minimum wave vector in the simulation to the wave vector termed the crossover point, \( q_{zz} \), at which \( S_x(q_{zz}) = S_z(q_{zz}) \).

Figure 7-8 illustrates how the characteristic length scale \( q_{zz}^{-1} \) as well as \( S_x(q) \) and \( S_z(q) \) are determined. Also plotted is \( q_{zz} \) normalized by \( \phi^{-1/d_f} \), which is the characteristic interparticle separation in a fractal structure with fractal dimension \( d_f \) [71,205], as a function of Mn*. The data also collapses onto a single master curve. \( q_{zz}^{-1} \), a measure of the width of the lobes in the butterfly scattering pattern, is solely controlled by the ratio of shear forces to the characteristic rupture force of individual bonds in the colloidal gel and also displays a non-monotonic dependence. For low Mn*, \( q_{zz} \) grows with the square root of the renormalized Mason number, reflected by the increasing width of the lobes of the scattering patterns in figures 7-2 and 7-4. The 1/2 power law growth arises from the evolving length scale of shear alignment in the 1-3 plane and is due the decreasing aggregate size with increasing shear: \( L_g \sim \text{Mn}^* -1/2 \). The complete breakdown of aggregates for \( \text{Mn}^* > 0.3 \) leads to rapidly declining values of \( q_{zz} \). As this occurs, the scattering power at small wave vectors is rapidly decreasing.

The alignment factor \( \tilde{A}_f \) takes a value between \(-1\) (corresponding to strict flow alignment) and \(1\) (indicating complete vorticity alignment). For all shear strengths, the attractive colloidal dispersions are vorticity aligned, that is \( \tilde{A}_f > 0 \), and the data are plotted as a function of Mn* in figure 7-9. \( \tilde{A}_f \) falls on a single master curve that shows a strong non-monotonic dependence on Mn*. The alignment factor measures the growing structural anisotropy and
Figure 7-8: Top: Illustration of the approach to measure $\tilde{A}_f$ and $q_{xz}$. $S_x$ (continuous) and $S_z$ (dashed) are the one dimensional averaged scattering intensities along the flow (x-axis) and vorticity (z-axis) direction, respectively. $q_{xz}$ is the largest value of the wavevector below which $\langle S_x \rangle > \langle S_z \rangle$ strictly holds. Bottom: The characteristic wave length $q_{xz}$ of vorticity anisotropy, normalized by the average particle spacing $\phi^{-1/d_f}$, as a function of $Mn^*$ for all $\epsilon$ and $\phi$ studied highlights the evolving length scale of anisotropic density fluctuations. Error bars represent 95% confidence intervals from three independent samples.

is independent of the large-scale integrity of the gel network dictated by $Mn^*/Mn_c^*$.

For values of $Mn^* < 0.3$, the degree of vorticity alignment in the dispersions grows with increasing shear as observed experimentally [168, 182]. For larger values of $Mn^*$ shear forces become much stronger than interparticle forces, and $\tilde{A}_f$ rapidly decreases as the aggregates are broken down to the single particle level. This change in response can be observed
Figure 7-9: The modified alignment factor $\tilde{A}_f(q = q_{xz}^{max})$ as a function of $Mn^*$ for all $\epsilon$ and $\phi$ studied indicates strong flow-induced anisotropy and displays a non-monotonic dependence on $Mn^*$. Also shown is the experimentally measured normalized alignment $A_f/A_{f,max}$ [196] and the alignment factor, $A_f$ [182], for two different adhesive hard sphere dispersions. Error bars represent 95% confidence intervals from three independent samples.

in the last column of figures 7-2 and 7-4 and is in agreement with recent experimental findings [159, 196]. The rapid decay in the measured alignment sets in for $Mn^* \sim O(1)$, when the stable aggregate size controlled by shear is much smaller than the system size, $N_g \ll N$. The reduction in the size of aggregates reduces the dispersion to a form akin to a hard sphere dispersion where vorticity alignment over such large length scales is not observed. This is responsible for the decrease in the overall alignment factor.

We compare the simulated alignment factor to the experimentally measured normalized anisotropy parameter $\tilde{A}_f/A_{f,max}$ for sheared dispersions of adhesive hard spheres (AHS) with $\phi = 20\%$, where the data also collapsed onto a single curve for all experimental conditions [196]. As the experimentally reported values are all normalized on the peak value, we do not know the absolute degree of structural alignment. We multiplicatively shift the peak in the experimentally measured alignment factor to match the peak in the simulations. The data exhibit remarkable agreement for Mason number preceding peak alignment. The alignment increases continuously with growing shear force until eventually, above a critical value of
the Mason number, the aggregates are broken down and the alignment factor decays. There is some disagreement between the data sets on the change in alignment beyond the peak. We attribute this to the absence of lubrication hydrodynamics in the simulations, which are necessary to reproduce the microstructure in sheared dispersions of hard spheres. The same horizontal shift for alignment was used in the inset of figure 7-7 to report the relative shear viscosity for the AHS dispersions of Eberle et al. [196].

Figure 7-9 also reports the measured alignment factor for another sheared AHS system [182], where $A_f$ is defined as in (7.6). If the angular deviations in the structure factor are a pure second harmonics, then the definitions (7.6) and (7.7) differ by a scale factor of 4. This is applied to the second set of experimental data. Because these experiments did not reach sufficient strain rates to see a decay in $A_f$, we shift their results multiplicatively to align the data with the simulations at small Mason numbers. The observed slight disagreement may come in the definition of the alignment factor. Both $\tilde{A}_f$ and $\tilde{A}_f/\tilde{A}_{f,max}$ reported by Eberle et al. [196] cover a broad range of measured length scales and the reported quantity is an aggregate of the anisotropy over these large scales. In contrast, Kim et al. [182] measure the alignment factor over a specific length scale, $q \approx (10a)^{-1}$. Alignment factors at different length scales or averaged over many length scales might show differing degrees of local structural anisotropy.

A direct observation in the 1–2 plane shows an enhanced scattering along the extensional axis ($\theta = 45^\circ$) indicating preferential particle buildup along the compressional axis ($\theta = -45^\circ$). At large length scales, there is structural anisotropy due to alignment along both the vorticity and the compressional axis. Similar observations were made in the above mentioned experiments [182,196]. We characterize alignment in the 1–2 plane by comparing the scattering intensity along the extensional axis, $S_+(q_x = q_y, q_z = 0)$, with that along the compressional axis, $S_-(q_x = -q_y, q_z = 0)$. A measure of the characteristic length scale is given by the inverse wave vector $q_{xy}^{-1}$, at which $\langle S_+(q) \rangle / \langle S_-(q) \rangle$ reaches its maximum value. This wavevector is plotted in figure 7-10 as a function of $Mn^*$ and normalized by $\phi^{-1/d_f}$. Again, $q_{xy}$ grows as $Mn^{*1/2}$, because increasing hydrodynamic forces are breaking down aggregates as they align. The colloidal gel is ordered on increasingly finer scales with increasing shear. As before, beyond $Mn^* \approx 0.3$, gel fluidization leads to a rapid loss of shear
alignment and reduction in large scale anisotropy and scattering power.

### 7.4 Hydrodynamic interactions as the origin of vorticity alignment

The presented simulations account for long-ranged hydrodynamic interactions between the colloidal particles through the Rotne-Prager-Yamakawa (RPY) mobility. Long-ranged hydrodynamic interactions are likely essential to observing flow instabilities of sheared gels in simulations. To confirm that this is indeed the case, the steady shearing simulations were repeated using freely draining Brownian Dynamics (BD). Figure 7-11 compares the 2D projections of the microstructure under steady shear deformations at the same conditions for simulations with and without hydrodynamic interactions. The difference in the simulation
Figure 7-11: The final structure of the colloidal dispersion for $\gamma = 500$ in the 1–2(top) and 1–3 plane (bottom) using the RPY approximation for long-ranged hydrodynamic interactions(left) and simple BD(right) for $\text{Mn} = 0.05$, $\phi = 10\%$ and $\epsilon = 0.1$. The effect of correctly accounting for long-ranged hydrodynamic interactions is striking - in BD the particles arrange themselves into sheets in the 1–2 plane, orthogonal to what is observed in experiments. In contrast, with long-ranged hydrodynamic interactions we observe anisotropic density fluctuations in the 1–3 plane and shear alignment along the extensional and compressional axes in the 1–2 plane.

outcomes is astounding. As discussed above, with long-ranged hydrodynamic interactions, the microstructure shows anisotropy characterized by the butterfly pattern as seen in experiments. Correlation lengths in the flow direction are much larger than in the vorticity direction and the aggregates formed are vorticity aligned. In contrast, neglecting hydrodynamic interactions yields highly periodic, intense scattering in the vorticity direction, which indicates ordered sheets of colloidal particles assembled densely in the 1–2 plane with a periodic spacing in the vorticity direction. This is confirmed by the snapshots in figure 7-11.
This mode of alignment is orthogonal to what is seen in experiments [168, 182, 195, 196]. Furthermore, the scaling relations for $Mn_\phi^*$ with $\phi$ and the scaling of $N_g$ with $Mn^*$ will also be sensitive to the hydrodynamic model chosen for the simulations. Since the shear force exerted on an aggregate depends on the hydrodynamic drag, without long-ranged hydrodynamic interactions we expect $L_g \sim Mn^*^{-1/(1+df)}$ since every particle in the aggregate acts as a point source of resistance and the drag coefficient on an aggregates scales as $\eta_s l^{df}$ [89]. In this case, $Mn^*_c \sim \phi^{(1+df)/(3-df)}$ and the stable aggregate size decays more weakly as $N_g \sim Mn^{*+df/(1+d_f)}$. Consequently, system size effects will be significant up to even larger values of $Mn^*$ and the rate of gel breakdown with $Mn^*$ will be underestimated in the absence of long-ranged hydrodynamic interactions.

While for much smaller system sizes, it was already speculated by Silbert et al. in 1999 that simulations that neglect hydrodynamic interactions would yield unphysical ordering under shear [188]. The unprecedented system sizes explored and analyzed in this work provide clear indication that shear induced anisotropy in gels is fluid mechanical in origin. It results from hydrodynamic coupling between aggregates, which stabilizes vorticity aligned flocs under flow. Consider the case of a particle doublet tumbling in steady shear flow for which it is known that vorticity alignment is a stable steady state [206]. With no forces acting along this neutral direction, the vorticity aligned structures persist. In BD, vorticity aligned clusters moving at different velocities in the imposed shear flow collide and realign. Asymmetric collisions pull the long axis of vorticity aligned flocs back into the 1–2 plane. This process sets up the periodic spacing between layers depicted in figure 7-11. With long-ranged hydrodynamic interactions, squeeze flows between vorticity aligned flocs prevent such collisions and stabilize the flocs against reorientation. This hydrodynamic effect is crucial for the stability of large-scale vorticity aligned density fluctuations in steady shear flow.

In using the RPY approximation for long-ranged hydrodynamic interactions, we only considered how the suspending fluid is transported in response to the total hydrodynamic force on particles and neglected the influence that higher order moments of the force density [32], such as the hydrodynamic stresslet might have on the breakdown of the colloidal network. Figure 7-12 shows that the degree of vorticity alignment and resulting large scale structural features are not affected by the next order approximation of long-ranged hydrodynamic inter-
Figure 7-12: Alignment factors for RPY simulations and simulations including forces, torques, and stresslets (FTS) at $\epsilon = 0.1$ and $\phi = 0.2$ show that the next order term in the hydrodynamic scattering series does not impact the dispersion structure. The inset shows contour maps of 2D density fluctuations in the 1–3 plane at $\gamma = 300$ and $Mn^* = 0.02$. The color intensity scale is the same as in the previous scattering patterns.

actions, accounted for in the Force-Torque-Stresslet (FTS) model. Hydrodynamic lubrication has also been neglected, which is not expected to alter the critical Mason number or affect the large scale anisotropies discussed here. However potentially, these lubrication forces could set the rate of compaction and the final shape of the particle flocs for $Mn^*/Mn^*_c \gg 1$, as considered for the results in figure 7-9.

7.5 Conclusion

Many experiments investigating the steady shear of weakly attractive dispersions have shown vorticity aligned density fluctuations. However, the simulations presented in this chapter are the first to replicate this phenomenon \textit{in silico}. The origins of this symmetry breaking phenomenon are no longer mysterious. Long-ranged hydrodynamic interactions are an essential physical component required to reproduce the characteristic butterfly patterns observed in
the flow–vorticity plane. The nonlinear rheology in the simulated dispersions and measures of their structural anisotropy such as the alignment factor are in quantitative agreement with the few experiments to probe both microstructure and rheology simultaneously.

To collapse the simulated data across different strain rates, bond strengths and temperatures, we introduced a single force scale: The most probable rupture force for the intercolloid bonds, \( f \), and the dimensionless parameter \( \text{Mn}^* \), which measures the ratio of hydrodynamic forces on particles to the most probable rupture force. Rescaling on this Mason number yielded master curves for the characteristic size of the vorticity aligned flocs and the virial contribution to the relative viscosity of the dispersions. By mapping the universal curves from simulations plotted as a function of the Mason number back onto physical parameters, our results provide one means of predicting structure and rheology in experiments.

A simple model that discriminates the response of a sheared colloidal gel based on a critical value of the Mason number \( \text{Mn}^*_c \) was developed. This critical value is system size dependent, and its value is important for comparing robustly experiments and simulations. For \( \text{Mn}^* < \text{Mn}^*_c \), shear is not strong enough to break the network into aggregates smaller than the system size in the confining dimension. Consequently, the network remains intact and the gel yields along fracture planes. The relative viscosity for simulations in this domain scales as the inverse square root of \( \text{Mn}^* \). For larger values of \( \text{Mn}^* \), shear breaks down the gel and we observe a steady shear response in a dispersion of vorticity aligned aggregates whose size is controlled by \( \text{Mn}^* \). While the results here were obtained starting from a fully formed gel at rest, additional simulations suggest that the microstructure of the system does not significantly change if the initial state is a fully dispersed colloidal dispersion. At high enough strain rates, we find that the stable state of the dispersion under flow is solely determined by the value of \( \text{Mn}^* \). Finally, we compared BD simulations with simulations accounting for long-ranged hydrodynamic interactions and showed that the squeeze flow between aggregates modeled by the RPY tensor stabilizes the vorticity aligned flocs. Neglecting long-ranged hydrodynamic interactions would yield scaling predictions for aggregate size different from that observed experimentally.

These findings are consequential for future computational models and experimental studies of attractive colloidal dispersions. Characterizing experimental systems in terms of the
renormalized Mason number Mn* will aid in identifying regimes of intact gels and network breakdown as well as describe the onset and evolution of nonlinear flow instabilities. Efforts to quantify this parameter as an inverse Bingham number, the ratio of hydrodynamic stresses to the yield stress, are a useful step in this direction. There are many fast simulation methods that account for hydrodynamic interactions in addition to the one applied here. We suspect each would resolve this nonlinear microstructural instability with similar fidelity. However, dynamic simulations of colloidal gels in the absence of hydrodynamic interactions can lead to spurious structuration and, as demonstrated repeatedly in this thesis so far, provide inadequate comparison with experimental results.

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Chapter 8

Shear-Induced Structure Formation Under Confinement

8.1 Introduction

Attractive colloidal dispersions display a great number of intriguing flow phenomena that are of great academic and industrial interest, including: yielding and jamming [200], shear-thickening [208] dynamical heterogeneity and aging [209], and pattern formation under shear of attractive systems [26]. In the previous chapter we have shown that long-ranged hydrodynamic interactions play a central role in stabilizing vorticity aligned flocs under steady shear flow, a general phenomenon observed in a wide range of dispersions [166, 168, 169]. Often these attractive dispersions are employed in novel devices requiring miniaturization or microfluidic applications, and therefore recent efforts have focused on exploring the effect of confinement on this flow instability. A dispersion is said to be confined in flow geometries where the gap size, \( H \), becomes comparable to the mesoscopic length scale characteristic of the fluid microstructure, \( L_g \) (see figure 7-6). In this steady-state regime bulk property measurements are not available and rheological data has been found to depend strongly on the gap width [171].

Strikingly, when sheared within a confined geometry, attractive flocs rearrange to form a highly ordered, striped pattern of log-rolling structures aligned along the vorticity direction. The spacing is consistent and periodic with a single characteristic wavelength. This
observation has been made for gels of anisotropic particles [210], attractive emulsions [165], nanotube suspensions [175], microfibrillated cellulose [211] and carbon black gels [170, 171] using either light scattering or various direct imaging techniques. Additionally, such vorticity alignment of the microstructure generally induces dramatic, often undesirable changes in the flow behavior, such as a pronounced shear-thinning or strong apparent slippage at the bounding walls. Clearly, an understanding of the mechanism by which confinement affects structure formation, also known as structuration, is of central importance in applications involving confined flows. While the phenomenon has been reported regularly, quantitative characterizations were often lacking. In some of these investigations, shear-induced log formation has been linked to the emergence of negative normal stresses [165,170], while other works proposed to interpret vorticity alignment and log-rolling as the consequence of an elastic instability that would occur locally within individual flocs [165,175]. However, clear experimental evidence for such interpretations and a detailed model establishing a link between an elastic instability and shear-induced structuration are still lacking. To date, no theory has been presented to explain the physical mechanism for the shear-induced pattern formation and that is able to predict both the characteristics and the apparent strain rate limits.

Grenard et al. [171] have reported an extensive analysis of the shear-induced structuration of carbon black gels in various geometries. They varied a range of control parameters such as the particle concentration, strain rate, and gap width to enable quantitative modelling of the vorticity alignment phenomenon. Both the steady-state diameter of the logs and the wavelength of the striped patterns were found to depend linearly on the height of the gap. The results were insensitive to both the gel concentration – suggesting that the forming cylindrical logs were compressible – and to the strain rate over a large range of values. For very low shear, the dispersion remained in a homogeneous solid-like state, while above a critical strain rate, the aggregates were separated and resuspended (cf. delayed yield and fluidization in 7.3.4). Even at low concentrations, when the number density of particles was too low to form complete rollers, the wavelength selection was evident. The same researchers found similar results for the shear-induced structuration of a dispersion of polyamide spheres and for an athermal model system consisting of an aqueous suspension of micron-sized glass
beads made attractive by oil capillary bridges [212]. This suggests a universality of this phenomenon over orders of magnitude in length scale, an additional challenge for any theory aiming to elucidate the origins of structuration.

This chapter proposes a physical mechanism for shear-induced pattern formation that can explain the observed characteristics. As explained in detail in 8.2, the superposition of planar Couette flow and flow between parallel plates due to a disturbance produces a set of periodically spaced hydrodynamic point torques co-rotating around stagnation points and leads to structuration. Dynamic simulations of confined attractive dispersions under shear discussed in section 8.4.1 confirm the important role played by long-ranged hydrodynamic interactions. We quantitatively recover the characteristic features of structuration observed in carbon black gels, polyamide and glass bead dispersions. Both simulation and experimental values are in good agreement with the proposed mechanism. We explain the origin of the limiting values for the concentration and strain rate for log-rolling in 8.4.2. Simulations of modulated initial structures discussed in 8.4.3 confirm that the system only admits one stable wavelength of periodicity.

Figure 8-1: Vorticity-aligned log-rolling structures observed in experiments by shearing attractive particles in confined gaps shown in the flow–vorticity plane. The horizontal corresponds to the flow direction and the vertical to the vorticity direction so that the gradient direction is perpendicular to the pictures. (a) Dispersion of colloidal carbon black particles in mineral oil (\(a = 180 \text{ nm}, H = 170 \mu\text{m}, \phi = 1.5\%\)) [171]. (b) Dispersion of non-colloidal polyamide particles in water (\(a = 9.4 \mu\text{m}, H = 1.5 \text{ mm}, \phi = 5\%\)). (c) Dispersion of non-colloidal hollow glass spheres in mineral oil bridged by water (\(a = 6 \mu\text{m}, H = 1.5 \text{ mm}, \phi = 3.1\%\)) [212].
8.2 Analysis

Two, force and torque free cylinders in Stokes flow between sheared parallel walls, feel by symmetry no relative force and thus any cylinder separation is neutrally stable and persistent [32]. Thus it may at first not seem like the periodic spacing of the observed cylindrical logs, i.e. the wavelength selection (see figure 8-1), can have a fluid mechanical origin. However, the log-rolling aggregates are composed of individual particles and so the cylinders are rough and easily perturbed. Therefore the symmetry argument which predicts no natural wavelength is invalid. Instead, the situation of a single rotating cylinder between stationary parallel walls is more helpful, as illustrated in figure 8-2. The flow field around the cylinder resembles a lid driven cavity in which the cavity is very deep [213]. Therefore, it contains a roughly periodically spaced set of counter rotating eddies moving along the channel that have a spacing of \( \sim 1.39H \), as shown by Moffatt [214].

If this flow field is superimposed with simple shear at the boundaries, the shear flow cancels out eddies that counter rotate and enhances the co-rotating eddies [215]. The centers of the co-rotating eddies act as stable stagnation points for the particle flow and are spaced \( \sim 2.78H \) apart, very close to what is measured in experiments. This suggests that during shear-induced structure formation the following process takes place, illustrated in figure 8-2.

As discussed in the previous chapter, in a sheared attractive dispersions a particle aggregate aligns along the neutral vorticity direction. When the first aggregate roller forms, particle number density localizes near the stagnation points to form other rollers that at steady state maintain their separation to neighboring rollers as given by the spacing of the stagnation points. Free particles in solution might cause fluctuations that can cause partially formed rollers to oscillate back and forth between adjacent stagnation points. Occasionally, as reported in the experiments, defects may arise in the structuration [171]. When an incomplete roller, an aggregate that does not span the entire vorticity length, already occupies one of the stagnation points, other rollers will bend in order to occupy two different stagnation points along their length (see figure 8-1). The mechanism to sustain that bending stress requires a force that is readily provided by the hydrodynamics through drag exerted by fluid flow in the gap between the rollers and the walls [216].
Figure 8-2: Schematic illustration of the fluid mechanical origin of shear-induced pattern formation (a) The flow field around a randomly formed particle aggregate or log (dark grey) resembles a lid driven cavity in which the cavity is very deep. Therefore, it contains a roughly periodically spaced set of counter rotating separatrices (cells with arrows) moving along the channel with periodic spacing. (b) If this flow field is superimposed with simple shear flow at the boundaries, the shear flow cancels out cells that counter rotate and enhances the co-rotating separatrices that have a table spacing of $\lambda \sim 2.78H$. (c) The centers act as stable stagnation points for the particle flow, where particles aggregate into further logs.

8.3 Simulation details

As in the previous chapters, we use Rotne-Prager-Yamakawa simulations (RPY) to model the shear-induced sturcturation of the attractive dispersions employing Lees-Edwards boundary conditions [61]. Confining walls are represented by a hexagonal close packed lattice of hard sphere particles connected to each other through permanent bonds. The walls interact hydrodynamically with particles of the colloidal dispersion and exert hard sphere repulsion.
at contact. This approach produces a very simplistic representation of confining walls, yet can effectively capture the complex hydrodynamic interactions of colloids near boundaries to first order [217]. There are three layers of particles in each wall to ensure sufficient bending stiffness under shear and to avoid buckling. Two walls in the flow-vorticity plane define the boundaries of the sheared cell and their separation, $H$ in number of particle radii, sets the height of the confining gap that is filled with attractive particles of volume fraction $\phi$. In order to resolve a statistically significant number of log-rolling aggregates, the aspect ratio $A_{xy}$ of the simulation box dimensions in the flow–flow gradient plane is kept at a constant factor of ten, resulting in an overall simulation box volume of $A_{xy}^2H^3$.

The short-ranged attraction is again modeled with an Asakura-Oosawa form [43]. Particles in the dispersion have mean radius $a$ and an imposed polydispersity of $d_a = 5\%$. The interparticle attraction is short-ranged with width $\delta = 0.2$ and depth $U_A$. Since logrolling has been observed in both Brownian and athermal systems, the thermal energy $kT$ of the particles must be inconsequential. In the simulations we proceed to study athermal dispersions with $kT = 0$, as this greatly accelerates the computational speed and allows us to explore a greater parameter space. As before, the strength of shear is varied by adjusting the Mason number, $M_n = 6\pi \eta a^2 \delta \gamma / U_A$, thereby tuning the strain rate $\gamma$. Under steady shear $M_n$ is held constant and the dispersion is strained for $\gamma = 600$ strain units. We study the effects of confinement in the parameter range: $H/a = 8 - 50$, $M_n = 10^{-2} - 10^1$ and $\phi = 4 - 22\%$, modeling $N = 10^3 - 10^5$ colloidal particles. All results are averaged over 3 independently generated samples for each combination of $\phi$, $H$ and $M_n$.

### 8.4 Results

#### 8.4.1 Characteristic size and spacing

Under all conditions the dispersions reach a steady-state after $\gamma \approx 100$. With the confining walls included in the RPY simulations we not only observe strong vorticity alignment but for a large range of shear strengths (see section 8.4.2) also the formation of well defined log-rolling structures with a periodic spacing, as shown in the snapshots in figure 8-3. Occasionally, we
detect defects in the pattern just as in the experiments, where a log maintains a bending moment as it is constrained by two neighboring stagnation points in its two halves, as depicted in the second snapshot.

Figure 8-3: Snapshots in the flow–vorticity direction of a simulation of short ranged attractive particles under shear forming a highly periodic array of vorticity aligned logrolling structures that span the gap height (confining walls not shown) for $\phi = 6\%, 12\%$ and $16\%$

In order to compare with the experimental results, we measure both the characteristic diameter of the aggregates in the flow–flow gradient direction, $d_{xy}$ and the wavelength of periodicity, i.e. the characteristic spacing between successive logs, $\lambda_x$. $d_{xy}$ is obtained by first computing the squared radius of gyration tensor of the logs:

$$R_g^2 = \left\langle \frac{1}{N_g} \sum_{i} r_i r_i \right\rangle,$$

where the average is computed over all clusters in the dispersion, $N_g$ is the size of each cluster and $r_i$ is the position vector of the particles such that $\sum_i r_i = 0$. $d_{xy}$ is then found from the smallest eigenvalue of the tensor as: $\sqrt{8\min \left( \lambda_g \right)}$, where the factor of eight stems from the relation of the diameter and radius of gyration of a solid cylinder. To extract $\lambda_x$ we compute the two-dimensional structure factor $S_{xz}(q) = S_{xz}(q_x, q_z)$ of the flow and vorticity coordinates of the colloidal particles using equation (3.1). We find the characteristic spacing by identifying the wavelength corresponding to the peak in $S_{xz}(q_x, 0)$ and define $\lambda_x = 2\pi / q_{x,max}$.

In figures 8-4 and 8-5 we plot $d_{xy}$ and $\lambda_x$ as a function of the gap height $H$ for a range of Mason numbers. In the experiments for carbon black gels and the glass beads, Grenard
et al. [171] have found that $d_{xy} \approx 1.05H$ and $\lambda_x \approx 2.5H$, indicated by the blue dashed lines in the figures. The red dashed line in figure 8-5 represents the relationship between $\lambda_x$ and $H$ expected from the theory on the spacing of the co-rotating eddies as described in 8.2.

For both quantities we recover a dependence on $H$ that is in very good agreement with what was observed in experiments. Clearly, as in the case of the experiments, the diameter of the logs is determined by the degree of confinement, the aggregates span the entire height of the cell and $d_{xy}/H \approx 1$. Similarly, the dependence of the spacing on the gap seen in the simulations, $\lambda_x \approx 2.55H$ matches that in the experiments very well. However, both simulation and experiments report a slightly weaker proportionality than the value of 2.78. This is expected, as Moffatt’s solution corresponds to a series of point torques as the source of the rotational streamlines as opposed to the colloidal aggregates with finite size. Potentially, perturbation analysis could be employed to identify higher order corrections of the flow field in response to a disturbance with a finite size, which may result in a smaller distance between co-rotating streamlines. Nonetheless, the strong linear dependence, the similar prefactors
observed in simulations, experiments and theory, and the fact that the mechanism is particle size independent, provide strong evidence that the shear-induced structure formation is hydrodynamic in origin. Naturally, simulations without an accurate representation of the hydrodynamic interactions between particles and the walls do not consistently recover any aspects of structuration.

8.4.2 Limiting values of volume fraction and strain rate

Just as in the experiments, we find that the steady-state features of shear-induced vorticity-aligned logs are independent of the imposed Mn for a large range of values. However, if the strain rate is too weak for a given confinement $H$, no structuration is observed, instead the aggregated dispersion is sheared in a solid-like state. This is the regime of delayed yield as described in chapter 7, in which shear forces are too weak to break apart the network and the gel can remain conductive and fulfill its engineered purpose. Equally, above a critical Mason number, $Mn_H$, the logs become unstable, they are broken down into smaller aggregates and
the dispersion is fluidized, the other extreme regime described earlier. In figure 8-6 we show the stability state diagram of shear-induced structuration and $\text{Mn}_H$ as a function of $H$, above which no structuration is observed. The boundary is well described by a power law that scales as: $\text{Mn}_H \sim H^{-1.4}$, again in very good agreement with the scaling seen in experiments for three colloidal dispersion, with vastly different sizes and characteristics: carbon black gels, glass beads with capillary bridges, and dispersions of polyamide spheres.

The scaling of the structuration boundary may be explained in terms of a simple force balance between the viscous drag force acting on an aggregate and the attractive forces that keep individual particles together. In chapter 7 we found that the critical Mason number for the onset of fluidization, when $d_{xy}/H < 1$, will scale as: $\text{Mn}_H \sim N^{-d_f/2} \sim H^{-d_f/2}$ – at fixed $\phi$ the number of particles is linear in the gap between the confining walls (see equation (7.5)).

Here, $d_f$ is the fractal dimension of the aggregates. Since we observe $\text{Mn}_H \sim H^{-1.4}$, this would suggest very compact aggregates with $d_f \approx 2.8$, in agreement with values observed of
strongly sheared aggregates measured previously [218,219]. In simulations, the aggregates and systems sizes we are able to explore are not sufficiently large to confirm this scaling. However, as discussed next, due to the large number density variations in the periodic pattern, the aggregates are very concentrated, which necessarily implies a fractal dimension close to the spatial dimension of 3, consistent with the observed scaling of MnH.

Finally, we study the effect of the value of \( \phi \), equivalent to the concentration of particles in experiments, on the characteristic size and spacing. We find that for a large range of values, \( 8\% \leq \phi \leq 20\% \), the results, shown in figure 8-7 are unchanged. This suggests that as the volume fraction is increased the logs become increasingly compact. The limits of the volume fraction range arise from considerations of particle volume conservation.

Above \( \phi = 20\% \) no structuration is observed as the dispersion is too dense: the network cannot break down into logs of size \( d_{xy} \) while also maintaining the hydrodynamically stable spacing \( \lambda_x \). The attractive particles can only be packed so tightly. The maximum random close packing of spheres that can be attained in a log is \( \phi_{rcp} \approx 63\% \) and consequently the maximum number of particles in a log of length \( A_{xy}H \) and diameter \( d_{xy} \) is \( A_{xy}Hd_{xy}^2\pi/4 \). Since the volume of particles is conserved, the maximum overall volume fraction can directly be related to \( \phi_{rcp} \) through: \( \phi_{rcp}N_LA_{xy}Hd_{xy}^2\pi/4 = \phi_{max}A_{xy}^2H^3 \), where the number of logs is \( N_L = A_{xy}H/\lambda_x \). Therefore the upper limit of the overall volume fraction for structuration cannot exceed:

\[
\phi_{max} = \phi_{rcp} \frac{d_{xy}^2\pi}{4\lambda_x H} \approx 20\%. \tag{8.2}
\]

In contrast, the lower \( \phi \) limit is set by the requirement that sufficient particles need to be present in the dispersion for them to aggregate and form a log that can span the depth of the confining plate. Indeed, below \( \phi = 8\% \) we do not observe continuous logs that span the entire vorticity dimensions, only shorter aggregates with smaller spacing and size in the flow–flow gradient plane, as shown in the left of figure 8-3.
Figure 8-7: $d_{xy}$ (left) and $\lambda_x$ (right) scaled on $H$ is independent of volume fraction for $8\% \leq \phi \leq 20\%$.

8.4.3 Dynamics of approach to the stable spacing

If the stagnation points of the eddies acting as attractors are indeed present and control the observed flow phenomenon, then the dispersion will naturally tend to evolve to the periodic spacing of the log-rolling structures exhibited at steady-state. This should hold true for a wide variety of starting conditions of the system. To illustrate this, we perform a set of simulations where we impose a spatially varying initial volume fraction in the simulation: 

$$\phi(x, \gamma = 0) = \phi_0 \left( \sin(2\pi x / \lambda_0) + 1 \right)$$

such that the overall particle volume fraction is fixed at $\phi_0$. By varying $\lambda_0$ relative to the expected final stable wavelength, $\lambda_s = 2.55H$, we can seed an initial periodic pattern and track the evolution of the instantaneous characteristic spacing in the pattern, $\lambda_x(\gamma)$, as a function of total accumulated strain in the dispersion. We explore the range $0.1 < \lambda_0 / \lambda_s < 4$ and plot the results in figure 8-8. Ultimately, irrespective of $\phi(x, 0)$ and $H$, the system evolves to the stable, periodic spacing of $\lambda_s$, observed earlier for $\gamma > 100$.

The exact path of the dynamic system to steady-state however is strongly dependent on $\lambda_0$. Specifically, two types of behavior are observed, determined by the size of the imposed density fluctuations relative to $\lambda_s$. For $\lambda_0 > \lambda_s$ the dominant spacing between particle rich regions decreases as it continuously approaches the final stable spacing with a power law of the form $(\lambda_x - \lambda_s) \sim \gamma^{-2/3}$, shown in the bottom of figure 8-8. In contrast, for
Figure 8-8: Top: The evolution of the instantaneous characteristic spacing $\lambda_x$ relative to the gap size $H$ as a function of total strain for a range of initially imposed length scales of density fluctuations, $\lambda_0$. Bottom: The absolute distance to $\lambda_s$ normalized on the initial distance, $\lambda_0 - \lambda_s$ as a function of total strain. The details of the dynamics on approach to $\lambda_s$ strongly depend on the initially imposed spacing $\lambda_0$.

$\lambda_0 < \lambda_s$ the behavior does not collapse onto a single, uniform curve. The trajectories of the characteristic spacing of the logs exhibit a peak as the colloidal dispersion homogenizes with strain and the periodic system size becomes the dominant wavelength. From this point, the dynamics of structuration proceed oblivious to the initially imposed wavelength and no collapse as a function of $(\lambda_x - \lambda_s)$ is possible. In the now uniform dispersion local fluctuations
lead to the growth of density variations in the flow direction and the characteristic spacing gradually develops with accumulating $\gamma$, similarly to any randomly mixed dispersions. These observations give further credence to the proposed mechanism that the characteristic spacing of the log-rolling structures is indeed due to the existence of stagnation points as a result of the fluid flow field between the sheared boundaries.

8.5 Conclusion

The stability of sheared attractive dispersions is a sensitive function of the confining geometry. For a wide range of strain rates shear induces the formation of vorticity aligned, periodically spaced log-rolling structures. In this chapter we studied structuration using dynamic simulations that account for the flow fields around the particles with high accuracy and approximated the hydrodynamic interactions near the walls using a boundary made of hard sphere particles. It was argued that the origin of log-rolling lies in the presence of periodically spaced co-rotating eddies centered on stagnation points. These are the result of the flow field perturbed by the presence of particle aggregates in the confined geometry. The computer model successfully recovers all features of log-rolling reported in the literature. The gap height $H$ between boundaries controls the characteristic size of the logs in the flow–flow gradient direction and the periodic wavelength of $2.55H$, measured for a range of particle concentrations and gap heights, is in excellent agreement with experimental measurements for different particle systems and the proposed mechanism. Additional simulations confirm that this spacing of the log-rolling structures is the sole steady-state that all sheared confined dispersions with imposed other initial wavelengths in particle number density evolve to. As seen in experiments, structuration is observed for a large range of initial particle concentration as the logs can compact up to the random close packing limit, and log-rolling is independent of the applied strain rate below a critical value relative to strength of attraction. The stable boundary demarcating structure formation from fluidization is a decreasing power law function of $H$ and is identical for three different experimental systems and the dynamic simulations performed here. The new insights gained about this intriguing phenomenon can be employed to design measures to avoid the breakdown of gelled
structures, crucial for example to carbon black gels in flow battery applications. Engineered log-rolling and controlled shear-induced structure formation also present new opportunities to manufacture nano-wires and related materials for electronic applications with tight size specifications.
Chapter 9

A Model for Hydrodynamic Instability in Freely Settling Colloidal Gels

9.1 Introduction

One of the most attractive engineering features of the space-spanning networks of attractive particle gels is their yield stress. Typically this is high enough to bear the material’s own weight, but low enough to give flowability during use [9, 220]. One key design requirement is that the particles must not sediment appreciably during the product’s "shelf life", which might range from weeks to years. Despite this restriction, a majority of colloidal gels, which contain non-density matched particles, exhibit various, undesired settling behaviors such as streamer formation and network collapse. In a range of other industrial scenarios, such as in conformance control during hydrofracking or industrial filtration, an equivalent state to mechanical compression occurs when the suspending fluid is pumped through the colloidal gel fixed in place and network collapse leads to unrestricted fluid flow [221, 222]. In either scenario, failure of the gel is equivalent to loss of utility of the product for these applications. Consequently, the ability to engineer and increase the stability of these elastic networks remains an important and prevalent issue for many industries.

The theory of sedimentation of attractive colloidal dispersions was developed by Buscall and White [223] describing the interplay of three forces that control the extent of sedimentation: the gravitational driving force, the viscous drag force associated with flow of liquid...
around and through the solid and the elastic stress developed in the network of particles. Sedimentation occurs when the gravitational force exceeds the local yields stress of the network resulting in three distinct zones of behavior: the supernatant, the falling zone, and the consolidating zone. The supernatant is the particle-free region above the network that is formed following the onset of sedimentation, whereas the consolidating zone at the bottom is the region throughout which the local yield stress exceeds the network pressure above it. In the falling zone, the gravitational driving force is balanced only by the viscous drag due to local fluid back flow and all particles settle freely at a rate that, in theory, can be directly related to the dispersion’s height profile. For a "tall" macroscopic sample, the majority of the particle network constitutes the falling zone and particles settle freely over experimentally relevant timecales.

Scientific studies of gravitational collapse of gels have in the last three decades focused on examining the settling behavior of model colloidal dispersions. New insights into colloidal aggregation and rearrangements under the influence of gravity could ultimately provide a thorough understanding of real aggregating systems [224], improve pressure-filtration driven fine solids separation processes [223], and elucidate the effects of gravity on the kinetics of arrested phase separation [25,225], and on diseases related to protein aggregation: sickle cell anaemia, Alzheimer’s disease and amyloid fibril growth [226].

Just as seen in industrial applications, the long-time structural integrity of an experimental gel, if not exactly density-matched, is constrained by the gravitational stress exerted by its own weight – the network may undergo gravitational collapse [225, 227, 228]. The most common and ultimate metric characterizing the macroscopic feature of the collapse process is the time evolution of the height profile, $h(t)$, of a gel. Measurements of $h(t)$ are used to determine the characteristic time scale of the process, $t_d$, and to quantify observed power law or exponential decays of height profiles [229–231]. The collapse dynamics of colloidal dispersions with long-ranged attractions, relative to the primary particle radius, are relatively well understood. Here, the network is transient, continuously coarsens and sediments over time exhibiting dynamics of a phase separation process analogous to spinodal decomposition [232]. In contrast, in the case of gels with short-ranged interaction, extensive experimental investigations performed in the past decades have shown that after a seemingly
arbitrary quiescent period, the dynamics of settling and compaction of the gel may proceed by widely different means depending on the range and strength of the particle interactions, and on the particle concentration within the gel [27].

"Strong" gels exhibit slow, uniform compression that halts once the yield stress of the now more compact network exceeds its own weight [233, 234]. In contrast, a "weak" gel initially shows a similar slow, uniform compression for a duration equal to the delay time $t_d$, before suddenly undergoing a rapid and catastrophic collapse. This has been observed in a wide variety of systems with short-ranged attraction, and the response appears to be a universal feature of "weakness" [224, 227, 228, 231, 235–239]. The distinction between strong and weak gels is purely based on the temporal dependence of the position of the meniscus separating the freely settling gel from the supernatant phase - a macroscopic observable, carrying very limited amount of information [230]. Microscopic insights of how the network evolves in time, how it transmits stress and what distinguishes strong from weak gels on the microstructural level are still elusive. Understanding how settling gels can be turned from "weak" into "strong" would facilitate the design of colloidal gel products with longer shelf lives and the ability to prevent delayed collapse within the desired user time frame.

Experimental colloidal gels already contain on the order of $10^6$ particles, and materials in actual industrial applications can contain several orders of magnitude more. Treating such large systems in a theoretical fashion therefore is, at present, only possible with approximate approaches, which describe the height profile via one dimensional transport equations [222]. Nonetheless, in the case of strong gels, a continuum model for the collapse rate has been developed based on the theory of poro-elasticity. It takes into account the resistance to compression arising from a combination of the fluid pressure and the elasticity of the network and successfully captures the full collapse behavior [233]. In contrast, for delayed collapse to date no widely accepted theoretical framework has emerged to account for the process [224, 231, 237]. Among other complicating factors and shortcomings, the poro-elastic theory fails due to the highly non-linear nature of the rapid collapse [233]. Alas, without a firm understanding of the collapse dynamics, the actual stability of many products remains unpredictable and uncertain.

While in general experiments cannot observe the microstructure of the catastrophic col-
lapse of these networks, a few careful studies have provided insight on the relationship between changes in microstructure and macroscopic collapse that can drive further theoretical development. Experiments conducted using dark-field microscopy imaging have reported landmark observations of the dramatic hydrodynamic instabilities that precede the sudden and rapid collapse [227,236]. The experiments observe the nucleation and growth of a large channel that is absent of particles, which provides a path for significant fluid back flow through it, a so-called "streamer". It grows in radius, and eventually also spans the height of the gel column, causing a small "eruption" at the interface between the supernatant and the settling gel, when catastrophic loss of network integrity occurs [240]. It has been hypothesized that compacting gel fragments breaking off from the top interface fall through the dilute network, and are responsible for the creation of the streamers that generate the hydrodynamic back flow and subsequent instability [231]. However, recent ghost particle velocity studies of collapsing gels that were able to measure the hydrodynamic velocity pattern before rapid collapse, have however reported the onset of two vertical streamers originating in the bulk of the sample [27]. They progressively expand, providing a path for the back flow of the fluid. Soon after, the breakdown of the gel becomes extremely fast, rapidly leading to the full disruption of the gel structure. It is thus evident, that fluid flow, the drag and hydrodynamic interactions exerted by the solvent on the particle network are crucial to understanding the collapse of freely settling gels.

Careful confocal microscopy studies of the association and dissociation processes of individual particles and gel strands in the network structure have also shown that there is a direct link between the macroscopic mean delay time \( t_d \) and the lifetime of an individual colloid-colloid bond [230]. As a result simple phenomenological models have been developed that describe the collapse process in terms of a number of sticky interparticle bonds undergoing sequential activated bond breaking and leading to a loss of network integrity. These models can relate the microscopic dynamics to the macroscopic settling with some success, albeit they have no ability to predict the onset of delayed collapse [228,230]. Additionally, no consideration has been given to the role of hydrodynamics in driving the collapse process – a theory explaining the observed dynamics in terms of controllable network parameters remains to be developed.
Given the experimental limitations and lack of comprehensive theories, dynamic computer simulations provide an invaluable tool to study the microscale dynamics of the hydrodynamic instability preceding collapse. A computer model is able to offer detailed particle level information of the entire gel network throughout the settling process, provided the simulation is able to capture the correct physical processes involved during collapse. In chapters 3 and 4 we have shown that the collective dynamics facilitated by the presence of long-ranged hydrodynamic interactions enable gelation and discussed the critical role these hydrodynamic forces play in setting the relaxation dynamics in chapters 5 and 6. Computer models that only include solvent-mediated hydrodynamic effects at the one-body level, i.e. Stokes drag, fail to reproduce the experimentally observed gel mechanics. This will especially be the case for the collapse of freely settling gels, which appears to be tripped by a hydrodynamic instability. For instance, in one example of the limited number of computer studies on settling gels, experimentally observed dense clusters that form during gel collapse have not been reproduced in simple Brownian Dynamics (BD) simulations lacking hydrodynamic interactions [231]. In another case, where gels were confined vertically in capillary tubes to within one gravitational length in experiments, BD simulations neglecting the fluid mechanics qualitatively reproduced the sedimentation profile. However, comparison with observations of bulk systems and the process of delayed collapse suggests that there is a fundamental difference in mechanism between these confined systems and bulk measurements of industrial relevance, which exhibit settling rates several orders of magnitude slower [241].

Here we present a comprehensive study of the hydrodynamic instability leading to collapse of freely settling colloidal gels, combining a new theory with computer simulation studies and comparison to experiments. We propose a microstructural model for the hydrodynamic instability comprised of nucleation and growth of streamers driven by network erosion from fluid back flow that leads to rapid gravitational collapse. The model relates the delay period prior to streamer blowup and gel collapse to various properties of the gel network, including particle volume fraction, the attraction range, interaction strength between particles relative to thermal forces, and gravitational strength. We study freely settling colloidal gels using Brownian dynamics simulations of attractive, hydrodynamically interacting particles in order to examine the formation and growth of these hydrodynamic instabilities. The settling
velocity and streamer volume are measured as they evolve over time, and a critical point for the onset of rapid growth in both quantities is identified. The settling process is well described by our theory. The model is also compared with two different experimental systems and is found to accurately predict the collapse dynamics.

This chapter is organized as follows. In section 9.2 we present a new microstructural model for network erosion and streamer growth in a model colloidal gel and arrive at a scaling law for the blowup time, i.e. the onset of catastrophic collapse as a function of network parameters. Next, in 9.3 we briefly describe the simulation details and in section 9.4 we present extensive results to validate our theory by comparing the model predictions to the collapse dynamics of freely settling gels in simulations and published experiments. Section 9.5 discusses a new conceptual framework for how to think about network stability, how the model can aid the engineering of these materials and concludes by highlighting potential areas of improvement.

### 9.2 Analysis and development of a model for network erosion

The model considers a system spanning percolated elastic gel network of attractive, spherical colloidal particles of radius $a$. The gel has a volume fraction $\phi$ and the tortuousness and porosity of this kinetically arrested material is characterized by the fractal dimension $d_f$. The short-ranged attractive well has depth $U_A$ and width $\Delta$. The particles have a thermal energy $kT$, density mismatch $\Delta\rho$ with the suspending fluid of viscosity $\eta_s$, and settle freely under the effect of a uniform gravitational acceleration $g$. This physical scenario is characterized concisely by only 5 dimensionless quantities, summarized in table 9.1.

In the free falling zone during sedimentation the network does not experience any effects from interactions with the supernatant interface and is unaware of the build up of the dense cake forming in the consolidating zone [223]. As the particles move downward, to conserve mass, fluid flows upward through the pores of the gel. Initially, under the imposed constant hydrostatic pressure gradient, $|\nabla p| = |g\Delta\rho|$, fluid flow will be uniform. Due to local density
fluctuations and further restructuring processes, local differences in the permeability of the network will be set up. This results in a burst in local fluid velocity relative to the mean and the fluid will nucleate a path of least resistance over a timecale $t_{\text{induction}}$. The increased volumetric flow rate of back flow through this initial channel exerts hydrodynamic drag on the particles in the network and leads to activated breaking of particle bonds, locally eroding the gel. This erosion leads to the widening of a largely cylindrical streamer and greater fluid back flow locally that further accelerates radial growth of the streamer. We describe the evolution of this streamer in terms of a cylindrical channel with growing radius $R$ over time, as shown in figure 9-1. The growth rate will depend on the net flux of particles that are eroded off the network into the channel and swept upwards with the back flow.

### 9.2.1 Growth of a critical streamer

To arrive at the radial growth rate of the streamer or channel, consider the transport process that move particles into the channel and the reverse process of attachment into the network. The evolution of the number of particles, $N_{Ch}$, in the cylindrical channel of height $L_{Ch}$ and radius $R(t)$ is given by the net flux:

$$\frac{dN_{Ch}}{dt} = J_{\text{in}} - J_{\text{out}} = 2\pi RL_{Ch}(j_{\text{in}} - j_{\text{out}}),$$

(9.1)
Figure 9-1: The micromechanical model considers a particle gel network freely settling in a gravitational field \( \mathbf{g} \). a) As the particles move downward, to conserve mass, fluid will flow upward through the pores (black arrows). b) Due to local density fluctuations the fluid will find a path of least resistance, where increased back flow will nucleate a streamer that spans the network. c) As the back flow increases, the fluid exerts drag on the particles at the interface leading to an activated rate of erosion and growth of the streamer. d) The streamer is modelled as a cylindrical channel with evolving radius \( R(t) \) in a gel of the same size \( L = L_{Ch} \). The growth rate will depend on the relative magnitude of particle fluxes into \( (j_{in}) \) and out of the channel \( (j_{out}) \).

where \( J \) and \( j \) are the rate and flux per unit area of particles into the growing channel \( (in) \) and out into the network \( (out) \), respectively. To the best approximation, for tall enough channels \( - L_{Ch} \) is large compared to the mesh size of the gel network \( - \) the number density of particles in the interior of the channel will be equal to its bulk value \( \phi \), so that the number of particles is related to the geometry of the channel through \( N_{Ch} = 3\pi R^2 L\phi / 4\pi a^3 \). When the channel spans the height of the network, \( L_{Ch} \) is unchanged over time and the one dimensional growth model of \( R(t) \) is:

\[
\frac{dR}{dt} = \frac{4\pi a^3}{3\phi} (j_{in} - j_{out}) = \frac{1}{n} (j_{in} - j_{out}) \tag{9.2}
\]

where \( n \) is the bulk number density of particles.
The flux of particles per unit area into the open channel is proportional to the surface number density of particles at the network-channel interface, \( \tilde{n} \), and the rate of particle bond breaking, \( k_{\text{break}} \):

\[
\dot{j}_n = d_1 k_{\text{break}} \tilde{n}.
\]

(9.3)

Note that throughout this chapter, \( d_i \) for \( i = \{1, \ldots, 6\} \) are unknown \( \mathcal{O}(1) \) scalar constants.

The boundary between the interior of the channel at bulk density \( \phi \) and the percolated gel network of fractal dimension \( d_f \) constitutes the "wall" of the streamer. For a fractal structure, the surface number density of particles attached to the network at this interface is

\[
\tilde{n} = \phi^{d_f/3} \frac{A}{a^2} \left( \frac{R}{a} \right)^{(d_f/3-1)}.
\]

As one would expect, for a compact structure with \( d_f = 3 \), \( \tilde{n} \) is independent of the radius. In the absence of an external force, we hypothesize that \( k_{\text{break}} \) is set by the Kramers escape time of a particle diffusing out of an attractive well of depth \( U_A \) and width \( \Delta \) [76]:

\[
k_{\text{break}} = \tau_K^{-1} = \frac{D}{a^2} \left( \frac{a}{\Delta} \right) \frac{U}{kT} e^{-U/(kT \Delta)} = \frac{D}{a^2} \delta^{-2} \epsilon^{-1} e^{-1/(d_3 \epsilon)},
\]

(9.4)

where \( D \) is the diffusivity of a particle of radius \( a \). The coefficient \( d_3 \) is included to account for the fact that the particles sit in a complex energy landscape in the gel network for which the barrier between bound and unbound states could be smaller \( U_A \) owing to elastic stresses stored intrinsically in the network during its formation. Due to the back flow of fluid through the channel, the particles at the interface will feel a hydrodynamic drag, due to the shear stress, \( \tau \), at the channel wall. This results in a relative force \( d_4 \tau a^2 / kT \) that stretches the interparticle bonds and accelerates the breaking process. This activated hopping leads to a higher rate of bond erosion. Assuming simple Poiseuille flow in the cylindrical channel the shear stress at the wall is related to the channel radius through \( \tau = |\nabla p| R/2 \) and \( k_{\text{break}} \) becomes:

\[
k_{\text{break}} = \frac{D}{a^2} \delta^{-2} \epsilon^{-1} e^{-1/(d_3 \epsilon) + d_4 |\nabla p| Ra^2 \Delta/(2kT)} = \frac{D}{a^2} \delta^{-2} \epsilon^{-1} e^{-1/(d_3 \epsilon) + R/R^*},
\]

(9.5)

\( R^* \) is an effective gravitational length, i.e. the characteristic length scale of the erosion.
process:

\[ R^* = \frac{2kT}{d_4a^2\Delta|\nabla p|} = \frac{8\pi a}{3d_4} \epsilon \delta^{-1} G^{-1}. \]  \hspace{1cm} (9.6)

It sets the characteristic pore size, beyond which the activated hopping dominates the bond breaking. The erosive flux of particles into the channel becomes:

\[ j_{in} = \frac{4\pi}{3} d_1d_2 \varphi^{d_f/3-1} R \left( \frac{R}{a} \right)^{d_f/3-2} \frac{nD}{a^2} \delta^{-2} \epsilon^{-1} e^{-1/d_3\epsilon + R/R^*}. \]  \hspace{1cm} (9.7)

The flux of individual particles currently in the bulk of the channel back onto the network is driven by diffusion according to:

\[ j_{out} = \frac{nD}{x} = \frac{nD}{R} f(\text{Pe}), \]  \hspace{1cm} (9.8)

where \( x \) is the thickness of the diffusive boundary layer at the wall of the channel and \( \text{Pe} \) is the advective Péclet number near the wall \( \text{Pe} = \tau R^2/\eta_sD = \frac{3\pi R^3a|\nabla p|}{kT} = \frac{9}{4} \epsilon G \left( \frac{R}{a} \right)^3. \) \( f(\text{Pe}) = 1 \) for \( \text{Pe} \ll 1 \) and \( f(\text{Pe}) \sim \text{Pe}^{1/2} \) when \( \text{Pe} \gg 1 \) [242, 243]. Except for very early times when the channel initially forms, the radius of the channel exceeds the primary particle size, \( R \gg a \), and \( \text{Pe} \gg 1 \), so that to first order:

\[ j_{out} = d_5 R \frac{nD}{a^2} \epsilon^{1/2} G^{1/2} \left( \frac{R}{a} \right)^{-1/2}. \]  \hspace{1cm} (9.9)

Note that \( j_{in} \gg j_{out} \) for \( R \gg a \) and to first approximation the flux of particles from the channel onto the network can be neglected: \( j_{out} \approx 0 \). Rescaling time \( t \) on the pure diffusive Kramers escape time, \( \hat{t} = tD \left( \Delta^2 \epsilon \right) e^{-1/d_3\epsilon} = t/\tau_K \), the model predicts the following evolution equation for \( R(t) \):

\[ \frac{dR}{dt} = \frac{4\pi}{3} d_1d_2 a \varphi^{d_f/3-1} \left( \frac{R}{a} \right)^{d_f/3-1} e^{R/R^*}. \]  \hspace{1cm} (9.10)

There are two competing effects that set the erosion of particles and the evolution of the radius of the channel. For fractal structures with \( d_f < 3 \), the quantity \( (R/a)^{d_f/3-1} \) suggests that the growth rate of \( R \) is slowed as \( R \) becomes larger as the total number
of particles eroded by the back flow is decreasing relative to the number of particles in the channel. In contrast, the term $e^{R/R^*}$, arises because the rate of bond breaking is exponentially dependent on the shear stress exerted by back flow, which itself is linear in $R$. Hence the activated rate of erosion grows exponentially with the channel radius. The result is that for $R > R^*$, the erosion process accelerates exponentially. More generally, such first order ordinary differential equations, which have a super-linear flux or grow rate, exhibit a finite-time blowup singularity [244].

In the case of this erosion model, we predict an exponentially dependent flux, an ultrafast type of super-linear growth, so that the channel radius will grow infinitely large at a critical point in time. This blowup time is defined such that: $R \to \infty$ as $t \to t_{\text{blowup}}$. This is the main result of our phenomenological model. At a certain critical point in time in freely settling gels a hydrodynamic instability occurs. The channel radius grows unstably to span the width of the gel. In practice, this corresponds to the streamer being of comparable size to the width of the container, as seen by Starrs et al. [227]) and large scale fluid back flow deconstructs the gel network. The solid is ripped apart and the gel rapidly collapses. Note, that due to the exponential growth profile, the fate of the network is determined long before $R$ reaches the system size. When $R \geq R^*$, the channel growth rate is exponential and catastrophic collapse is unavoidable. However, macroscopically the radial growth of the channel may not manifest itself in a dramatic increase in the settling velocity of the network’s top interface until $t$ is right near $t_{\text{blowup}}$.

To explain this observation consider that for an incompressible Newtonian suspending fluid the settling velocity of a gel, and therefore the velocity of the interface will be proportional to the average fluid back flow velocity, $\langle u_f \rangle$, driven by the constant pressure gradient $|\nabla p|$ across the network. Here, $\langle u_f \rangle$ is the average volumetric flow rate of fluid back flow through the intact gel and the streamer channel. For simplicity, the intact gel network can be thought of as a porous Darcy medium with permeability $\kappa$, whereas the streamer is a cylindrical channel with Poiseuille flow, as before.

The fluid velocity through the gel network is given by:

$$u_f^D = -\frac{\kappa}{\eta_s} \nabla p.$$  \hspace{1cm} \text{(9.11)}
The total flow rate through the medium with cross sectional dimension $L_{Ch}$ and a cylindrical pore of radius $R$ within it is $Q_f^D = -\left(L_{Ch}^2 - \pi R^2\right)$ $\frac{\kappa}{\eta_s} \nabla p$. In the cylindrical channel the velocity profile is: $u_f^{Ch} = -\frac{1}{4\eta_s} \nabla p \left(C - r^2\right)$, where $r$ is the radial position and the constant $C$ is set by the boundary condition at the cylinder wall $r = R(t)$. At the interface, the boundary condition will be highly dependent on the exact fractal structure of the network. This can be captured at lowest order by introducing an inverse Navier's slip length $\lambda_f$ so that at the boundary [245]: $u_f^{Ch} (r = R(t)) - u_f^D = -\lambda_f \frac{d u_f^p}{d r}$.

Therefore the resulting parabolic flow profile inside the channel is:

$$u_f^{Ch} = -\frac{1}{4\eta_s} \nabla p \left(R^2 - r^2 + 2\lambda_f R + 4\kappa\right), \quad (9.12)$$

with a volumetric flow rate: $Q_f^{Ch} = \frac{\pi R^2}{8\eta_s} \nabla p \left(R^2 + 4\lambda_f R + 8\kappa\right)$. Thus the average fluid back flow velocity over the pore and porous medium as the gel settles is given by:

$$\langle u_f \rangle = \frac{Q_f^{Ch} + Q_f^D}{L_{Ch}^2} = -\frac{1}{\eta_s} \nabla p \left[ \kappa + \frac{\pi}{8} \left(\frac{R}{L_{Ch}}\right)^2 \left(R^2 + 4\lambda_f R\right) \right] \quad (9.13)$$

For the majority of the growth process, the channel size will be negligible compared to the overall size of the porous medium, i.e. $R/L \ll 1$. The rate of collapse of the gel is therefore limited by the back flow of the fluid through the solid network. It is controlled by $\kappa$, yielding a uniform settling profile of the top interface as if there were no growing channel [233]. However, as the settling proceeds and $t \rightarrow t_{\text{blowup}}$, $R$ will grow rapidly and the channel cross section will become significant, $R/L \sim \mathcal{O}(1)$. The second term in equation (9.13) will dominate the fluid back flow velocity. Consequently, the interface velocity will appear to increase rapidly as the size of the channel becomes comparable to the size of the gel network. Therefore $t_{\text{blowup}}$ sets the timecale for the onset of macroscopic collapse.

### 9.2.2 Finite-time singularity in streamer growth

A closed form expression for the finite-time singularity, or blowup time of the streamer predicted by the model can be found by specifying the initial value for the radius of the
channel, $R(\hat{t} = 0)$:

$$t_{\text{blowup}} = d_6 R^{2 - df/3} \Gamma(2 - d_f/3, R(0)/R^*) \phi^{1 - df/3},$$  \hspace{1cm} (9.14)

where $\Gamma(a, x) = \int_x^\infty s^{a-1}e^{-s}ds$ is the incomplete Gamma function and $d_6 = \left( d_1 d_2 4\pi/3 \right)^{-1}$.

Our model predicts that the finite-time singularity is intrinsic to all freely settling colloidal gel networks. However, it is only observed in practice when certain conditions for the ratio of timecales dictating collapse are met, as discussed in detail in section 9.5.

As mentioned earlier, a further feature of the collapse process as described by the model is the initial nucleation of the channel or streamer over a positive induction period. $\hat{t}_{\text{induction}}$ is the time required for stochastic fluctuations to form a path of least resistance for the fluid back flow. When there is no initial seeded streamer present in the gel, $R(\hat{t}) = 0$ for $0 \leq \hat{t} \leq \hat{t}_{\text{induction}}$, and it follows that:

$$\hat{t}_{\text{induction}} = \hat{t}_{\text{blowup}} - d_6 R^{2 - df/3} \Gamma(2 - d_f/3, 0) \phi^{1 - df/3} \approx \hat{t}_{\text{blowup}} - 0.9 d_6 R^{4/3} \phi^{1/3},$$ \hspace{1cm} (9.15)

when $df = 2$. Given a macroscopic sample size the likelihood of a necessary fluctuation to be present is almost certain.

As discussed in section 9.5.2, heterogeneities within the initial gel may form from other processes beyond mere thermally driven restructuring [24]. These can have a number of origins, including falling debris that accumulates at an interface [231], external forcing fields [230], or included bubbles. Once a streamer is born with initial size $R(0)$, the growth rate is universally described by (9.10) and the final stages of breakup leading to collapse are identically captured by the model, with $R^*$ being the only controlling parameter. Notice that $\hat{t}_{\text{induction}} \ll \hat{t}_{\text{blowup}}$ and so the time point for the macroscopically observable onset of collapse will be determined by the singularity predicted by the model.

Because the incomplete Gamma function takes on values $[0, 1]$, the behavior of the blowup time is dictated by the network parameters in the model:

$$t_{\text{blowup}} \sim \tau_D \phi^{1 - df/3} \delta^{df/3} \epsilon^{3 - df/3} \epsilon^{1/d_3} G^{df/3 - 2}.$$  \hspace{1cm} (9.16)
The only unknowns are the scalar coefficient of proportionality and the coefficient associated with Kramers hopping process, \( d_3 \). This is a clear prediction of how the point in time where the hydrodynamic instability and collapse occurs relates to properties of the gel network. These are the adjustable material parameters that are available to engineer stability into the particulate network. We next test the model validity using extensive computer simulations and comparisons to published experimental data in the next section.

### 9.3 Simulation details

In order to study hydrodynamic instabilities during gel collapse and observe the breakdown of the network, the effects of fluid flows and hydrodynamic forces have to be modelled accurately in large scale simulations. Therefore, in this chapter we only employ Rotne-Prager-Yamakawa simulations and do not report comparisons with any BD simulations. Freely settling, attractive, hydrodynamically-interacting, hard sphere colloidal particles of size \( a \) in a solvent of viscosity \( \eta_s \) are simulated. The simulations contain \( N = 216,000 \) particles having a volume fraction \( \phi \), which sets the size of the cubic simulation box, \( L \). \( N \) has been selected to avoid any system size effects and to be able to resolve large scale structural changes. Other choices of aspect ratio, including stretched and flattened gel columns, have been investigated and do not affect the simulation results that follow. Any interactions with the container and other potential wall effects are neglected. While the interactions with walls may influence collapse \[220\] the onset of the hydrodynamic instability occurs far from any boundaries in the freely settling regions of gels and effects of the sample geometry may be insignificant \[27\]. Zero volume flux boundary conditions on the simulation box ensure sedimentation models the free falling zone \[223\], where the gel network is freely settling. Note that as a consequence the bottom of the container and the compacting cake region, shown previously to play no role in collapse, are ignored. Furthermore the processes at the top surface of the gel and the role of the meniscus in inducing collapse are not under study. The simulation can be viewed as modeling micron sized colloids and a millimeter sized gel cross section deep inside a sedimenting network that is in a state of free fall.

The short-ranged attraction is modeled once again through an Asakura-Oosawa form \[43\],
Figure 9-2: Snapshots of a simulation with $\delta = 0.1$, $\epsilon = 0.05$, $G = 0.5$ and $\phi = 20\%$. Differently colored layers are purely illustrative and indicate initial particle positions in the gel to guide the eye through the breakdown of the network during free settling shown for a particle depth of $30a$. The dispersion gelled over $500\tau_D$ in the absence of gravity and has a structure characterized by $d_f = 2.05$. a) At $t = 0\tau_D$ gravity is turned on in the simulation and the network begins to settle. b) After initial uniform settling, a single cylindrical streamer nucleates (bottom center). c) The streamer is both growing radially and its height spans the bottom half of the network. d) At the onset of settling rate increase ($t = t_{\text{crossover}}$) the streamer spans the height of the gel. e) The streamer continues to grow radially, filling the entire sample, destabilizing and altering the uniform settling of the network. f) There is complete loss of network integrity as entire aggregates are ripped off the gel.
with a range of attraction, $\delta$, and where the pairwise depletion strength at contact, $\epsilon$, sets the network strength from the athermal limit, $\epsilon = 0$, to a hard sphere dispersion, $\epsilon \to \infty$, as described in chapter 2. The uniform gravitational load on all particles is tuned through the gravitational Mason number, $G$. We study the settling systems over a range of volume fractions: $\phi = 5 - 50\%$, strengths: $\epsilon = 0.01 - 0.2$, Mason numbers: $G = 0.1 - 1.0$, and attraction ranges: $\delta = 0.075 - 0.15$ (see table 9.1 for definitions of all dimensionless quantities).

Initially, the dispersion is allowed to gel for 500 bare diffusion steps, $\tau_D = 6\pi \eta_s a^3 / kT$ in the absence of gravity. Use of the box counting method determines the Minkowski-Bouligand dimension $[79]$, $d_f$, for each gel, which characterizes the meso-scale structure and tortuous nature of the random network. Note that due to the finite system size and finite particle size the gels are not true fractal objects over all length scales. At time $t = 0$ we introduce a finite gravitational Mason number $G$ and observe the process of free settling over a simulation time of $2500G/\epsilon \tau_D = 2500\tau_G$, where $\tau_G$ is the characteristic settling time, the time it takes a single particle to settle its own radius in bulk fluid. As the network moves downward, fluid back flow, particle erosion and the eventual failure of the network are observed. All reported simulation results are averaged over 3 independently generated samples for each combination of $\delta$, $\epsilon$, $G$ and $\phi$.

### 9.4 Results and model validation

To assess how well the model captures the process of gravitational collapse we compare it to both results of simulations of settling gels and experimental observation. In 9.4.1 we present the results of the parametric sweep in terms of the network parameters. In section 9.4.2 we show the dynamics for a range of seeded channel sizes. While good agreement between theory and simulations is necessary, to be certain about the model validity, it has to reproduce collapse dynamics observed in experiments. Finally, in 9.4.3 we present comparisons with two published experimental studies.
Figure 9-3: The average network settling rate $u(t)$ normalized by the initial rate $u(0)$ as a function of simulation time in units of bare diffusion time $\tau_D$ for increasing $G$ with $\delta = 0.1$, $\epsilon = 0.05$ and $\phi = 20\%$. The onset of rapid growth in settling rate, $t_{\text{crossover}}$, is the point in time where the power law growth at a given $G$ intersects the plateau of uniform settling $u(t) = u(0)$, marked by the two dashed lines.

### 9.4.1 Comparison with simulations of freely settling colloidal gels

The colloidal gel networks in the simulations all exhibit gravitational collapse during free settling. While the exact time point at which this occurs strongly depends on the network parameters $\delta$, $\epsilon$, $G$ and $\phi$, all gels eventually experience a hydrodynamic instability and fail catastrophically as shown in figure 9-2. Initially, the network settles uniformly under its own weight and fluid flows upwards through the gel pores. After an initiation period, a single streamer nucleates in the gel. This streamer grows radially as individual particles and small clusters are eroded and swept upwards with the back flow. The streamer then grows and spans the height of the settling gel. There now exists a continuous channel for fluid back flow and the entire network is destabilized as the streamer rapidly expands in the radial direction. Eventually, portions of the gel compact, network integrity loss occurs and large domains of the gel move independently both up and downwards. The gel is no more and the network has undergone catastrophic collapse.
We quantify this process using two independent metrics, the evolution of the network settling velocity and the growth of the streamer volume over time. The average network settling velocity, $u(t)$, is measured by computing the velocity of the center of mass of the gel in the frame of an external observer, the lab frame as opposed to the frame of zero volume flux, the Lagrangian perspective, for all gels under study (note that we exclude the velocity of particles that are not attached to the percolated structure). Figure 9-3 shows this network settling velocity normalized on its initial value, $u(0)$, as a function of dimensionless simulation time for increasing values of $G$ and constant $\delta, \epsilon$ and $\phi$. The data exhibit three distinct regimes of settling. As seen, the network begins to settle with a constant initial uniform velocity. Then at a certain point, the velocity grows as a power law in time until it enters the third regime, where it reaches a new plateau of the settling velocity with $u_{\text{final}}/u(0) \sim \mathcal{O}(10)$, consistent across all gels studied. Interestingly, Starrs et al. [227] also observed a ten-fold increase in their velocities from initial settling to final collapse.

In agreement with visual observations, a stronger gravitational force results in an earlier onset of the power law growth in settling velocity. We term the transition to power law growth the crossover time, $t_{\text{crossover}}$, and identify it in each simulation as the point where the best-fit power law line intersects the initial settling velocity, as illustrated in figure 9-3 by the dashed lines. $t_{\text{crossover}}$ changes by orders of magnitude depending on the values of the network parameters, but eventually a transition to an increasing settling velocity and final plateau is observed for even the strongest gels studied here.

In parallel with the measurements of the network settling velocity, we track the growth of the overall streamer volume for each gel, employing an approach similar to the box counting method. In short, the total volume of boxes containing no particles is counted. By excluding the fraction of boxes that measure the empty pore space in the remaining intact network, we can compute the volume of the streamer (see appendix A for details). Figure 9-4 plots the evolution of the streamer volume $V(t)$ normalized on the simulation box volume for the same set of gels as in figure 9-3. Initially there is no noticeable streamer present, i.e. its volume is below the sensitivity threshold of the measurement technique. At a certain point in time, which decreases with increasing $G$, $V(t)$ exhibits a power-law growth, very similar to the behaviour exhibited by $u(t)$. Again, it is possible to extract a crossover time, $t_{\text{volume \ crossover}}$, using
Figure 9-4: The growth of streamer volume normalized on the simulation box volume plotted as a function of simulation time for increasing $G$ with $\delta = 0.1$, $\epsilon = 0.05$ and $\phi = 20\%$.

The same method as before. In figure 9-5 we plot $t_{\text{crossover}}^{\text{volume}}$ vs. $t_{\text{crossover}}$ and find that the two timescales are identical to within the measurement errors. The acceleration of the settling network and its ultimate collapse is directly correlated with the nucleation and subsequent growth of the streamer in the gel in accordance with the mechanism described by the model.

The crossover time measured in simulations marks the beginning of the collapse of the gel, after which the network rapidly loses its integrity. While the dynamic simulations exhibit the same qualitative behavior as described by the model, it remains a question whether (9.16) can predict how $t_{\text{crossover}}$ depends on the network parameters. Figures 9-6–9-9 separately examine the dependence of $t_{\text{crossover}}$ on $G$, $\phi$, $\delta$ and $\epsilon$, respectively.

The effect of increasing gravitational Mason number for three different network strengths and volume fractions is demonstrated in figure 9-6. The dashed line indicates the expected scaling behavior as given by (9.16) for a network with fractal dimension $d_f = 2$: $t_{\text{blowup}} \sim G^{4f / 3 - 2} = G^{-4/3}$. Indeed for a range of gravitational Mason numbers for all three conditions the crossover time exhibits the scaling that the model would predict. Small deviations from the $-4/3$ scaling are expected as the measured $d_f$ for the gels in these simulations range...
Figure 9-5: The onset of rapid growth in streamer volume $t_{\text{volume}}^{\text{crossover}}$ is in direct parity with the onset of power law growth in network settling velocity, $t_{\text{crossover}}$, which supports the model's premise that streamer nucleation and growth is a cause for loss of network integrity in settling gels.

between 1.7 – 2.3. For large gravitational forces ($G > 1$) a different mechanism controls the network collapse. $t_{\text{crossover}}$ appears independent of the gravitational Mason number and the situation is one of weakly aggregated clusters settling freely [224].

Next the dependence of $t_{\text{crossover}}$ on the volume fraction is analyzed for two different combinations of $\delta$, $\epsilon$ and $G$ along with the expected scaling behavior from the model, assuming $d_f = 2$: $t_{\text{blowup}} \sim \phi^{1/3}$. The crossover time exhibits roughly the model behavior for a large range of volume fractions, shown in figure 9-7. As the fractal dimension is especially sensitive to $\phi$, it is no surprise that $t_{\text{crossover}}$ deviates slightly from the $\phi^{1/3}$ scaling. The model prediction breaks down for $\phi > 30\%$, at which point the starting material cannot be considered a gel, but instead approaches the properties of a colloidal glass. Clearly, other restructuring processes dominate settling in these dense structures [9].

Similarly, the critical time exhibits the model predicted dependence on the attraction range, $t_{\text{crossover}} \sim \delta^{d_f/3}$, shown in figure 9-8. For the values of $\delta$ investigated here, the Noro-
Figure 9-6: The measured onset of rapid network collapse, $t_{\text{crossover}}$, is plotted as a function of $G$, while the other network parameters are held constant. The collapse dynamics exhibit the power law behavior predicted by the micromechanical model for networks with $d_f \approx 2$. Each data point is the average of three independent simulations and error bars represent 95% confidence intervals.

Frenkel extended law of corresponding states suggests that the thermodynamic restoring forces for these dispersions will all be vary similar [113]. To maintain the short-ranged nature of the colloidal bonds however, $\delta$ could not be increased above this narrow range since it known that the evolution of the collapse dynamics are markedly different for gels with long-ranged attractions [232]. So, agreement with the model should be considered tentative.

Finally, we consider the effect of the network strength $\epsilon$ on $t_{\text{crossover}}$. Since (9.16) suggests both a power law and exponential dependence on $\epsilon$, figure 9-9 plots $\log \left( e^{d_f/3} t_{\text{crossover}} / \tau_D \right)$ vs. $\epsilon^{-1}$. Note, in the model, the proportionality constant modulating the strength of attraction, $d_3$ is left undetermined. Indeed there appears to be a linear relation between the timescale of collapse of the network and the Kramers escape rate, as previously observed experimentally [230]. The slope of the best-fit line for all three combinations of $\delta$, $G$ and $\phi$ indicates that the best choice for the constant is $d_3 = 5.6$ and the crossover time exhibits the
Figure 9-7: $t_{\text{crossover}}$ is plotted as a function of $\phi$, while the other network parameters are held constant. Each data point is the average of three independent simulations and error bars represent 95% confidence intervals.

relationship with $\epsilon$ that the model predicts. While we cannot provide a physical explanation for this particular value, it is a result of the simplified approach to approximate the network erosion in terms of the bond breaking rate or escape probability of individual particles from the attractive well. For very large attractions, $\epsilon \leq 10^{-2}$ a small deviation from the predicted scaling is observed. Section 9.5.2 discusses possibly reasons for this and ways to improve the model.

It appears that the phenomenological model adequately predicts the dependence of the critical timescale in dynamic simulations on the dimensionless parameters and captures the essential features of collapse. Equation (9.14) gives a quantitative prediction for the critical blowup time to within a scalar constant, provided only the values of the five dimensionless network parameters. In figure 9-10 we plot the measured $t_{\text{crossover}}$ vs. $t_{\text{blowup}}$ and find a direct parity between the two quantities. Here, every data point is an individual combination of $\delta$, $\epsilon$, $G$ and $\phi$ and the calculated $d_f$, averaged over three independent simulation runs. Given this linear relationship, the slope of the best-fit line through the data can be used to obtain
Figure 9-8: $t_{\text{crossover}}$ is plotted as a function of $\delta$, while the other network parameters are held constant. Each data point is the average of three independent simulations and error bars represent 95% confidence intervals.

the missing scalar constant for the model, arriving at the final result:

$$t_{\text{blowup}} = 540\tau_D \phi^{1-d_f/3} \delta^{d_f/3} e^{3-d_f/3} e^{1/(5.6\epsilon)} G^{d_f/3-2}.$$  \hfill (9.17)

For a colloidal gel (9.17) can be applied to calculate the point in time where the hydrodynamic instability occurs, leading to rapid collapse.

### 9.4.2 The effect of a finite initial channel radius

During the analysis of the computational model results presented so far, when relating $t_{\text{crossover}}$ to $t_{\text{blowup}}$ it was implicitly assumed that $t_{\text{induction}} \approx 0$, i.e. $R(0) = R_0 = 0$ and that a streamer is nucleated immediately after the start of the simulation. This is reasonable since $t_{\text{induction}} \leq t_{\text{blowup}}$ and the dynamics are controlled by the finite time singularity.

However, as mentioned previously, an initial vertical channel might already be present in the gel network at $t = 0$. Or, on observing a gel undergoing collapse, the initial starting point itself may not be well defined in an actual system, especially since in experiments colloidal...
Figure 9-9: The measured onset of rapid network collapse, $t_{\text{crossover}}$, is plotted as a function of $\epsilon$, while the other network parameters are held constant. Each data point is the average of three independent simulations and error bars represent 95% confidence intervals. The slope of the best-fit line yields the scaling coefficient $d_3$ that sets the relevant strength of attraction, $d_3 \approx 5.6$.

dispersions do not gel independently from the influence of the gravitational field they are in. Regardless, the model permits a solution for $t_{\text{blowup}}$ when assuming an initial condition $R_0 \neq 0$ for (9.10). Intuitively, it is expected that catastrophic collapse in a gel with a channel present will occur sooner than in an unperturbed gel. Indeed, using the result in (9.14) the model prediction for the shortened finite-time singularity relative to the unperturbed case is found to be:

$$\frac{t_{\text{blowup}}|_{R_0}}{t_{\text{blowup}}|_0} = \frac{\Gamma \left(2 - d_f/3, R_0/R^* \right)}{\Gamma \left(2 - d_f/3, 0 \right)},$$

The ratio of Gamma functions is guaranteed to be less than unity, regardless of the value of $d_f$, in agreement with the intuitive expectation. The only controlling parameter is the value of the initial channel radius $R_0$ relative to $R^*$ and this ratio is predicted to be independent of $\phi$.

To test this prediction we conduct an additional set of simulations of freely settling gels where a vertical cylindrical channel of height $L$ and radius $R_0$ devoid of particles is seeded at
Figure 9-10: The onset of rapid network collapse, $t_{\text{crossover}}$, as measured in dynamic simulations is plotted as a function of the model prediction $t_{\text{blowup}}$, computed for the combination of $\delta$, $\epsilon$, $G$, $\phi$ and $d_f$ used in the respective simulation run. Each data point is the average of three independent simulations with the same unique combination of parameters in the parameter space and error bars represent 95% confidence intervals. The model predicts the collapse dynamics to within a scalar coefficient, the value of which is given by the slope of the best-fit line through the data (dashed line).

The center of the simulated gel at $t = 0$. The parameter $R_0/R^*$ is varied systematically. This is achieved both, by increasing $R_0$ relative to the overall size of the gel, and separately, by decreasing $R^*$. Remember, the gravitational length depends on $\delta$, $\epsilon$ and $G$ so that the effect of varying network parameters is directly incorporated. Because of the exponential growth, in order to resolve the decrease in blowup time, we explore a parameter range of 2 orders of magnitude in $R_0/R^*$. As long as the initial pore is small relative to the system size, the assumptions of our model should hold and the onset and dynamics of collapse should only be determined by the radius of the streamer. In each simulation the crossover time with a seeded pore is measured and compared to the corresponding crossover time in an unseeded gel at the conditions. We plot their ratio in figure 9-11 along with the prediction of (9.18).

We find an excellent agreement between (9.18) and the simulation results. For small
Figure 9-11: The measured values of $t_{\text{crossover}}$ in the presence of a seeded hole at $t = 0$ relative to the timescale of an unperturbed sample are plotted as a function of the relative seeded channel radius $R_0/R^*$ for different $\phi$. $R^*$ is set by a combination of $\delta$, $\epsilon$ and $G$. Each data point is the average of three independent simulations with the same unique combination of parameters in the parameter space and error bars represent 95% confidence intervals. The measured values are in good agreement with the model prediction of (9.18) using a value of $d_f = 2$ (dashed line).

seeded channel sizes the collapse times decrease only minimally, whereas for $R_0/R^* \sim \mathcal{O}(1)$, $t_{\text{crossover}}|_{R_0}$ falls off due to the dominating exponential growth, as expected. Simulations show that the seeded channel acts instantaneously as a streamer as it provides a free path for fluid back flow when the gel is settling. Particles on the network-streamer interface are immediately eroded off the network and swept upwards. Soon after settling is initiated the streamer begins to grow as the back flow propagates radially outwards and larger fractions of the gel network disintegrate. This provides further evidence that the growth of a streamer in a settling gel is indeed the cause for the rapid instability leading to collapse. As we have shown, the predictions of the simple model of streamer growth agrees well with the collapse dynamics observed in simulations for a large range of parameter values and initial gel states.
## Table 9.2: Experimental parameters of collapsing gels as found in [227] and [27].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Starrs et al.</th>
<th>Secchi et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attraction width $\Delta$ (nm)</td>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>Attraction strength $U_A$ ($kT$)</td>
<td>6.5</td>
<td>12</td>
</tr>
<tr>
<td>Density mismatch $\Delta \rho$ (g/cm$^3$)</td>
<td>0.26</td>
<td>1.14</td>
</tr>
<tr>
<td>Particle radius $a$ (nm)</td>
<td>196</td>
<td>90</td>
</tr>
<tr>
<td>Solvent viscosity $\eta_s$ (mPa s)</td>
<td>2.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Temperature $T$ ($^\circ$C)</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>Volume fraction $\phi$ (-)</td>
<td>0.2</td>
<td>0.04</td>
</tr>
</tbody>
</table>

### 9.4.3 Comparison with experimental observations

So far it was shown that the model correctly captures the mechanism of collapse seen in dynamic simulations. Here we show that our theory also describes the gel collapse behavior in two vastly different experimental systems by fitting available data of the evolution of the observed streamer radius as a function of time to our model.

Starrs et al. [227] studied a system of polydisperser PMMA particles that were induced to gel in the presence of polystyrene depletants in a tetralin and cis-decalin solvent blend. In so-called "weak" gels streamers formed, and the gel exhibited catastrophic collapse following a hydrodynamic instability. The weak gels were differentiated from "strong" gels considered in the study by the lack of hydrodynamic instability and the observation of steady, poro-elastic compression rather than a dramatic collapse. Secchi et al. [27] looked at an aqueous dispersions of spherical MFA particles, a copolymer of tetrafluoroethylene and perfluoromethylvinylether. Depletion interactions were induced by the addition of a surfactant that forms globular micelles leading to a short-ranged attraction. Here, the onset and subsequent radial growth of streamers destabilizing the network was also observed. In both cases, snapshots depicting the increasing size of the streamer with time were included by the authors, providing two experimental data sets for the evolution of the streamer radius, $R(t)$. Table 9.2 provides the parameters for the two experimental systems.

Assuming an initial pore size, $R(0) = 0$, equation (9.10) at time $t$ has the solution:

$$
\frac{t_{\text{blowup}} - t}{t_{\text{blowup}}} = \frac{\Gamma(2 - d_f/3, R(t)/R^*)}{\Gamma(2 - d_f/3, 0)},
$$

(9.19)
which has three parameters: $t_{\text{blowup}}$, $R^*$, and $d_f$. As seen earlier, the model predictions are not sensitive to the value of $d_f$ in the range of $1.7 - 2.3$ and so in the absence of any further information from the experiments, we assume that $d_f = 2$ for both networks, a typical value for dilute colloidal gels [9]. Therefore, it remains to obtain a best-fit of (9.19) to the two experimental data sets to extract the parameters $t_{\text{blowup}}$ and $R^*$. Figures 9-12 and 9-13 compare the experimentally observed streamer radius to the best-fit model predictions. The measured dynamics for both experimental systems follow the model quite well, and table 9.3 provides the best fit values for $t_{\text{blowup}}$ and $R^*$.

![Figure 9-12: Comparison of published data [227] (open squares) and the best-fit prediction of the model (dashed line).](image)

The quantities $t_{\text{blowup}}$ and $R^*$ can be estimated from experimental parameters independent of the model fit. Using the values of the experimental quantities in table 9.2, $t_{\text{blowup}}$ and $R^*$ are computed directly using (9.6) and (9.17) assuming again $d_f = 2$ and taking the coefficient $d_4 = 1$. These estimates are reported in table 9.3. In the case of the work by Starrs et al. [227] the best-fit values for both parameters are in good agreement with what can be computed a priori. This would suggest that the proposed model subsumes all essential factors contributing to streamer growth and can accurately describe the dynamics.
Figure 9-13: Comparison of published data [27] (open circles) and the best-fit prediction of the model (dashed line).

of network erosion and collapse. In contrast, the estimates of $R^*$ and $t_{blowup}$ for the other example are an order of magnitude larger than the corresponding best-fit values. $R^*$ exceeds the dimensions of the gel and $t_{blowup}$ exceeds the observation window reported [27]. Since the dynamics are well captured by the best-fit, this would indicate that there is no seeded pore in the gel. Instead, we conclude that there is some uncertainty in the experimental parameters. While we have assumed that the characteristic building blocks of the gel in the experiments are individual MFA particles, Secchi et al. [27] note that there is strong evidence to suggest that the particles move in aggregated clusters. As the model displays a high sensitivity to the size of particles within the gel (see 9.5.1) the value of the hydrodynamic radius $a$ can significantly impact the quality of the predicted blow-up time. Indeed, using $a = 3 \times 90\text{nm}$ as the characteristics size, we recover estimates of $R^*$ and $t_{blowup}$, shown in the last row of table 9.3 that are both physically reasonable and agree with the best-fit values.

As a result of the exponential growth rate of the streamer radius, the value of $R(t)$ and the dynamics in the vicinity of blowup are very sensitive to $t$ and change rapidly, as seen in figures 9-12 and 9-13. While $t_{blowup}$ and $R^*$ depend on the experimental parameters and are
Table 9.3: Values of $t_{\text{blowup}}$ and $R^*$ as found from the model best-fit to the experimental data and their estimates based on details of the experimental parameters in table 9.2. In the case of Secchi et al. [27] estimates are based on the primary particle radius $a$ and three times the size for $a$ (see third row).

<table>
<thead>
<tr>
<th></th>
<th>Starrs et al.</th>
<th>Secchi et al.</th>
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<tbody>
<tr>
<td></td>
<td>$t_{\text{blowup}}$ (min) $R^*$ (mm)</td>
<td>$t_{\text{blowup}}$ (min) $R^*$ (mm)</td>
</tr>
<tr>
<td>Best-fit</td>
<td>593±11 4.85±0.1</td>
<td>34±2 2.02±0.15</td>
</tr>
<tr>
<td>Estimate from Parameters</td>
<td>623 4.94</td>
<td>986 22.5</td>
</tr>
<tr>
<td></td>
<td>37 2.51</td>
<td></td>
</tr>
</tbody>
</table>

unique to each study, (9.19) suggests that $\Gamma(2-d_f/3, R(t)/R^*)$ will exhibit a universal linear dependence on the distance to blowup, $(t_{\text{blowup}} - t)$. Figure 9-14 plots the experimentally measured streamer radii as a function of distance to blowup, and we observe indeed a one-to-one parity as expected from theory. This indicates that the model for streamer growth contains the necessary dynamics to understand and track the hydrodynamic instability leading to the collapse of the network in both types of colloidal gels.

![Figure 9-14](image_url)

Figure 9-14: Parity plot of the predicted and the measured distance to blowup (see text for details) for the two very different experimental systems. The theory is able to capture the underlying collapse dynamics well, independent of the experimental details.
9.5 Discussion

Gravitational collapse is an intricate process during which the microstructure of the gel undergoes numerous changes. These culminate in the break down of the hierarchical network structure and macroscopic structural failure. A number of experiments observe a "sudden" collapse in which a slowly and steadily moving interface suddenly accelerates and falls. The model we have presented describes in detail a process through which erosion of the network and the growth of streamers in a freely settling gel can lead to such a perceived sudden change in material properties. We have shown that these significant rearrangements in the microstructure do not manifest themselves on a macroscopic level until a time point very close to a singularity in the streamer growth. From the point of view of applying this model to real gels, a good theory of gravitational collapse has to be able to explain and predict the ultimate parameter of interest, \( t_{\text{blowup}} \) as presented here. The model we have proposed relates \( t_{\text{blowup}} \) to the engineerable network and solvent properties. Both dynamic simulations and comparisons with previously published experiments have confirmed that the model reproduces quantitatively the collapse dynamics of these gels.

9.5.1 Stability: a competition of two timecales

The timecale \( t_{\text{blowup}} \) is an intrinsic property of each freely settling gel network and characterizes how long the gel remains stable before hydrodynamic back flows erode network integrity. The proposed model suggests that this hydrodynamic instability will occur at a definite point in time, after the beginning of free settling. According to the model, no gel is immune to this instability – yet stable gels can be engineered. Certain strong gels remain stable against gravitational stresses for years, while only compacting mildly [220, 230, 233]. As described earlier, these strong gels exhibit a slow uniform compression under gravity. By compacting steadily in time, the gel becomes denser and strong, allowing it to fulfill its engineered purpose. The slow condensation process is well described by the theory of poro-elasticity, in which forces responsible for mechanical compression balance with the drag due to uniform fluid back flow and the elastic stresses within the compacting network. Poro-elastic settling
occurs over a characteristic timescale [233]:

\[ t_{\text{poro-elastic}} \sim \frac{\eta h_0^2}{\kappa E} \sim \frac{\eta h_0^2 \phi^{2/(3-d_f)}}{a^2 E}, \]  

(9.20)

which measures the time required for the compressing network to develop sufficient strength to support its own weight. Here \( h_0 \) is the initial height of the gel, \( E \) is its elastic modulus and the permeability \( \kappa \sim a^2/\phi^{2/(3-d_f)} \) with an \( \mathcal{O}(1) \) prefactor, will depend on the porosity of the network.

All networks in which a density mismatch between fluid solvent and solid particles is present, will initially sediment in this manner. However, in weak gels the process of poro-elastic compression is interrupted by the formation of streamers which leads to subsequent rapid settling. In this framework then what distinguishes strong from weak gels under gravity is the ratio of two timescales:

\[ T = \frac{t_{\text{blowup}}}{t_{\text{poro-elastic}}}, \]  

(9.21)

which provides a criterion for deciding whether a network will exhibit poro-elastic compression or streamer mediated collapse. When \( T \gg 1 \) a colloidal network will exhibit characteristics of poro-elastic compression. Initially, much of the network will be in a mode of free settling which can produce streamers, but the timescale for streamer formation, \( t_{\text{blowup}} \) is too long for such pores to form. Instead, the settling will come to an end when the compressed gel has developed enough strength to support itself. In contrast, for \( T \ll 1 \) the gel will settle, but does not densify quickly enough. Instead, streamers nucleate within the gel, eliminate any elastic resistance through erosion of the network, and result in rapid collapse.

This criterion is also supported by experimental observations. In addition to the set of experiments on weak gels, Starrs et al. [227] also studied the collapse of gels with stronger interparticle attractions. These gels did not collapse, but instead underwent steady, poro-elastic compression, which arrested in a more compact, and stable state. The timescale for this consolidation process here was reported to be \( t_{\text{poro-elastic}} = 40 \) hours. For the set of experimental parameters corresponding to this strong gel, our model predicts \( t_{\text{blowup}} \approx 44 \) hours so that \( T > 1 \). From this ratio of timescales, we would expect that the gel should remain intact. In contrast, consider the value of \( T \) anticipated for the weak gels that were studied
The completion of poro-elastic compression was not observed in the experiments, but we estimate $t_{\text{poro-elastic}} \approx 32$ hours using the assumption that the network elastic modulus decreases in proportion with the strength of the interparticle attraction. From fitting to the model and independent calculation, we determined that $t_{\text{blowup}} \approx 10$ hours. Consequently $T < 1$, and the gel is expected to be unstable.

Equations (9.16) and (9.20) show that $t_{\text{blowup}}$ and $t_{\text{poroelastic}}$ are only functions of material properties. Therefore it should be possible to evaluate $T$ in advance and predict the stability of a proposed experimental system without any detailed experimentation. Especially useful is understanding how specific parameters influence this ratio. For instance, consider the dependence on particle size. We have shown that $t_{\text{blowup}} \sim a^{d_f - 5}$. Because the elastic modulus of the network depends on its mesh size, we conclude that $E \sim a^{-3}U_A/kT$, and the poro-elastic timescale is linearly proportional with the particle radius: $t_{\text{poro-elastic}} \sim a$. Therefore the ratio of timescales depends on $a$ as: $T \sim a^{d_f - 6}$, suggesting that the stability of colloidal gels is strongly controlled by the primary particle size. In fact, decreasing the particle size will drive the network toward pure poro-elastic compression. This ratio also helps to explain why the stability of a gel is so sensitive to changes in $U_A$ [227]. From (9.17), the streamer formation time most significantly depends exponentially on $U_A$, while from (9.20), the poro-elastic timescale scales with the inverse of $U_A$. Consequently, $T \sim e^{U_A/(5.6kT)}$, and small changes to the strength of attraction in $U_A$ will lead to large changes in the ratio of timescales that significantly alter the stability of the gel. Finally, the hydrodynamic instability is dominated by the activated erosion process driving the streamer growth and is thus sensitive only to intrinsic properties of the network. In contrast, the poro-elastic compression timescale depends on the initial height of the gel. Thus, $T \sim h_0^{-2}$, so that taller gels are more susceptible to the hydrodynamic instability. In laboratory experiments, this is known and shorter gels, which may appear stronger, are often avoided when studying the collapse phenomena [227, 233, 235, 237].

In many practical applications, whether to avoid the collapse of yogurt in a cup or the failure of a gel proppant in a fracking channel, the required shelf life of the material, $t_{\text{shelflife}}$, is a well defined finite quantity. In terms of the model discussed here, the requirement of stability translates to the blowup time exceeding the application or user defined shelf life.
Figure 9-15: The stability state diagram marks the continuous region of stability (shaded) and distinguishes it from catastrophic instability beyond. In the stable region $t_{\text{blowup}}$ is larger than the desired $t_{\text{shelflife}}$ of a given product. Here only a three dimensional cross section of the entire parameter space is shown.

Thus, even if it is not possible to choose parameters such that $T_{\text{collapse}} \ll 1$ and achieve indefinite stability, at least material properties can be tuned with the goal of an extended lifetime so that $t_{\text{shelflife}} \leq t_{\text{blowup}}$, which defines the desired minimum value for the blowup time and the relevant stability criteria, $T_{\text{shelflife}} = t_{\text{blowup}} / t_{\text{shelflife}} > 1$. This way it can be ensured that the hydrodynamic instability will only set in once the gel network has fulfilled its role past its required lifetime. In practice then, given a use case defined constant $\min(t_{\text{blowup}}) = t_{\text{shelflife}}$, (9.17) determines how the values of the network properties must be chosen. In figure 9-15 we present a three dimensional subset of the four dimensional parameter space of $\delta$, $\epsilon$, $G$ and $\phi$, which represents the trade-offs that have to be considered in material engineering of stable gel networks. In the continuous stable region characterized by high volume fractions, low gravitational Mason numbers and high network strengths, the blowup time exceeds the desired shelf life of the specific product under consideration. The boundaries between the stable and unstable region will be highly non-linear, but are defined by the respective parameter pairs and the model predictions. Such a stability diagram enables rational selection of materials or engineering of colloidal interactions, both of which...
involve trade-offs in the space of network properties.

Consider yet another application, where colloidal gel networks are used in processes of sludge reduction and dewatering. In such contaminated site remediation programs, the material essentially acts as a filter used to halt the flow of the pollutants while the whole network is under fluid driven compression [221]. Here, the effective gravitational Mason number, $G$, is controlled by the process operator through the choice of $\nabla p$. This parameter specification ultimately determines the time point at which the network becomes unstable. In this application, the other relevant timescale is the duration of the dewatering process [246], $t_{\text{process}}$, controlling the total amount of sludge that is processed. The maximum rate at which the water can be treated safely without any network failure will be set by the ratio of these two timescales, $T_{\text{process}} = t_{\text{blowup}}/t_{\text{process}}$ and the same stability criteria apply. The proposed model may aid in selecting the correct operating conditions for such remediation activities.

### 9.5.2 Model improvements

As we have shown, the model adequately predicts the observed dynamics in simulations and explains the onset of sudden collapse in experiments. However, in developing the model a few simplifying assumptions had to be made: chiefly about the number of particles within the streamers that form, the process of activated bond breaking, the fractal nature of the gel, and the boundary conditions imposed on the network. Here we revisit some of these assumptions and discuss future work to resolve remaining issues.

During the growth of the streamer, as particles are broken off the fractal network at the channel interface and swept upwards due to back flow, local gradients in particle concentration will be established and the distribution of particles within the streamer should not be uniform as assumed when constructing (9.2). However, as discussed during the model development, for a sufficiently large control volume around the streamer and the porous gel network, the number density of particles in the interior of the streamer due to mass conservation will have to be equal to its bulk value. In this context, a sufficiently large control volume means a streamer whose height is very large compared to the typical mesh size of the gel network. On that length scale, the expression used for the number of particles on the surface of the network will be valid, and mass conservation will ensure that the model
predicts a consistent number of particles entering the streamer per unit time.

The growth of the streamer is driven by the viscous drag exerted by the fluid back flow resulting in activated bond breaking of individual interparticle bonds, which drives the growth in $R$. The bond breaking rate, which scales as: $e^{-\left(1/\varepsilon\right)^{1/d_3}}$, reflects the particle escape probability from the potential well. We assumed that the effective activation energy setting this rate will not be the strength $U_A$ of a single interparticle bond, but an undefined scalar multiple. A value of $d_3 > 1$, which was obtained from the simulation results in figure 9-9, would suggest that the bonds are weaker than in the case of an escape from a single pairwise bond. In fact, when a bond in the gel is broken, a single particle or a cluster of particles may detach from the network and enter the streamer. As a result, it is probably more useful to think of the activated escape rate as being set by several independent bond breaking events, any one of which might free some portion of a cluster to follow the back flow. Thus the $1/d_3$ power in the proposed Kramers hopping expression allows for more attempts at bond breakage per unit time. To more precisely account for this effect, we would need to track the statistics of clusters entering the streamer in order to weight the flux by the appropriate number of particles detaching from the gel, which remains to be done in future work.

The five dimensionless parameters in table 9.1 fully characterize the model gel. Of these, the fractal dimension $d_f$ is the most difficult to control as it is a characteristic of the kinetically arrested percolated network and how that network was formed. In principle this could be predicted, but in practice it is more likely to be measured once the gel has formed. In experiments, $d_f$ is obtained from the power-law growth of the structure factor at low wavelengths, whereas in simulations due to the finite system size, as is the case here, the box-counting method is employed as a surrogate. Thus, $d_f$ is not known in advance and (9.17) cannot be predictive in the strictest sense. For the model to be useful, a value of $d_f$ has to be assumed, which can be justified by prior experience with the specific gel under study and the fact that for random percolated gels the fractal dimension is typically in the range $d_f \approx 1.7 - 2.3$ [9]. In fact, when fitting the model to the experimental streamer growth data, in the absence of any measurements, the assumption of $d_f = 2$ resulted in good agreement. Clearly, an accurate knowledge of $d_f$ could improve this and result in a better match between parameter estimates and the model predictions. We were able to validate
the scaling of the blowup time by studying $t_{\text{crossover}}$ as a function of $\delta$, $\epsilon$, $G$ and $\phi$ in figures 9-6-9-9. However, (9.17) is not especially sensitive to the value of $d_f$ due to the limited range of variability, and we could not control $d_f$ explicitly. Therefore, dependence of the model on the value of $d_f$ remains to be confirmed.

Since the model as presented here considers a freely settling gel, it neglects the processes occurring at both the top and bottom interfaces in contact with the supernatant and compacting region, respectively. As shown by Buscall and White [223] and repeatedly observed in experiments, the majority of the collapsing gel is in a mode of free fall and macroscopically unchanging before collapse [27]. Since the particles at the bottom of the gel are unable to support the weight of the network above it, a concentrated foot grows at the bottom of the container by continuous, slow compaction. However, this process is part of the poro-elastic compression, and it is largely agreed that the compaction occurs independent of the events leading to the hydrodynamic instability in the freely settling region.

In contrast, it has been suggested that the origins of delayed collapse are related to the free surface at the top of the gel. Interactions between the meniscus and the container walls may delay the settling as the network is pinned to the top interface. The surface tension holding the colloidal particles at the air-solvent interface can be significant with energy per unit surface area on the order of: $\sigma \sim 10^3 - 10^6 kT/a^2$ [247]. In contrast, particles in the layers beneath the gel surface are held in place solely by interparticle bonds that cannot support the tension due to the weight of the gel network hanging below. Thus, while the forces on the particle contact line can suspend a layer of particles at the interface [27, 231], the entire network is not pinned and can detach readily without producing a detectable delay preceding collapse.

However, it may be the case that the interface with the supernatant has a role to play in seeding an initial streamer through the network. Colloidal particles at the air-solvent interface are in constant motion owing to thermal motion [248]. Recently it has been observed that particles coalesce and form concentrated clusters at the top interface [231]. These fragments compact, break off and can fall through the network to create the channels whose growth our model could describe. Indeed, the model presented here lacks an exact description of how an initial channel is seeded. Gels are kinetically arrested materials with structural
heterogeneities. Therefore, it was assumed that streamers form from natural density fluctuations. It is entirely plausible and fully compatible with the model that paths of preferred fluid back flow are seeded by other restructuring and aggregation processes, for example: bubbles which rise through the network, or foreign objects and debris falling through the gel [230, 231, 240]. As shown in section 9.4.2 with controlled simulations, a seeded initial channel radius $R_0$ produces the same collapse dynamics, which are universally described by the phenomenological model.

Furthermore, consider the network stability in a range of industrial applications, where very often, the choice of formulation or processing history of the gel will result in a number of holes and channels that extend across the sample and may be distributed randomly. In such a case the overall stability of the network will be set by the growth rate of the streamer expanding the fastest. Thus the onset of the hydrodynamic instability can only be determined with knowledge of the heterogenous state of the gel. However, as long as the distribution of initial channel sizes can be estimated reasonably accurately, a distribution of blowup times can be inferred and a survival probability used to characterize the sample lifetime.

For colloidal networks, gravitational collapse is a complex phenomenon with many dynamic processes occurring throughout the network simultaneously. The micromechanical model described here sheds light on one central aspect, the rapid growth of streamers leading to the instability and collapse of freely settling gels. Nonetheless, new approaches are required to be able to study the settling processes at the gel boundaries and free interfaces. In the freely settling mode hydrostatic equilibrium cannot be established, so the eventual arrest of the settling process will be intimately coupled to the interactions with the container. While dynamic simulations provide a useful tool to interrogate the microstructure, as discussed here, it is the interplay of gravity and hydrodynamics that leads to the intricate settling scenarios and hydrodynamic interactions have to be accurately incorporated in these computer models. Modelling hydrodynamic interactions in colloidal dispersions near interfaces and walls is a challenging task. Ongoing projects aim to develop new fast computational tools for simulations with lubrication forces and of particles near walls in order to shed light on the evolution of the gel microstructure in a wide range of applications [60, 249].
Future investigations should seek to conduct new experiments and computer modeling of the same colloidal gels in parallel in order to enable more careful comparisons of the detailed dynamics between model predictions, experiments and simulations.

9.6 Conclusion

The catastrophic collapse of colloidal gels settling under their own weight remains a major engineering challenge in many areas of industry and science, from personal care and foodstuffs through industrial proppants to biomedical applications. We have shown with models and simulations that the sudden transition from slow uniform settling to rapid and complete loss of network integrity has a unified origin in these applications. Over the last decades, careful experiments have advanced an understanding of the restructuring preceding collapse: bond rearrangements and breakage lead to the formation of open streamers through the network. Our simulations have enabled the direct observation of fluid back flow through these streamers and the effects of the viscous drag that the back flow exerts on the gel network. These stresses erode the network and lead to a hydrodynamic instability that terminates in failure of the gel.

This chapter has introduced a new phenomenological model for the evolution of streamers embedded in a freely settling colloidal network. The model describes the process of streamer growth due to fluid back flow, which strips particle from walls of the streamer. The rate of erosion increases exponentially with the streamer radius so that the model exhibits a finite-time blowup: At a finite point in time, the radius of the streamer is infinite. We correlate this point in time with the onset of catastrophic failure in the gel. This timescale is related directly to dimensionless groups describing the network: the ratio of buoyant forces to network strength, the particle volume fraction, the strength of inter-particle bonds relative to the thermal forces acting on the particles, and the relative range of the pairwise attraction.

Extensive Brownian dynamics simulations of hydrodynamically interacting, freely settling, attractive colloidal gel networks show that the rapid increase of the streamer volume in the gel coincides with increased settling velocities during collapse. The time for onset of accelerated settling scales with network parameters as predicted by the model, and we have
demonstrated a direct parity between the model blowup time and this critical time point in simulations. The extensive parameter sweep conducted in simulations is used to determine the unknown constant of proportionality of the phenomenological model, which is necessary to make quantitative predictions. The predicted evolution of streamer radius with waiting time is also shown to successfully capture the collapse dynamics for two different published experimental systems.

The model considers a gel in a mode of free settling and neglects the effects of container walls and the processes occurring at both the top and bottom interfaces in contact with the supernatant and compacting cake region, respectively. Regardless, the model accurately predicts the dynamics of the hydrodynamic instability leading to collapse in freely settling gels. We find that the critical feature demarcating strong from weak gels under collapse is the ratio of the poro-elastic compression timescale to the finite-time blowup. Since both processes are intrinsic to any gel under gravitational load, strong gels are the ones where poro-elastic compression proceeds to completion before the onset of the hydrodynamic instability. Therefore the key to achieving longer shelf lives is to engineer and tune network properties until the blowup time exceeds the poro-elastic timescale, the user defined shelf life of the product, or the relevant process time of the application. With the concepts presented in this work and the newly developed model, stability of colloidal networks can be rationally engineered.
Chapter 10

Conclusion

"All models are wrong, but some are useful" — George E.P. Box [250]

This thesis constitutes a systematic approach to studying the role of hydrodynamic interactions in setting the microstructure and macroscopic properties of attractive colloidal dispersions and networks. The strategy adopted here was to employ novel computational models to investigate the kinetic arrest, viscoelastic response and failure mechanisms of colloidal gels. This was paired with the development of phenomenological theories to explain experimental observations and provide quantitative predictions about mechanical behavior. Mindful of the fact that the real world cannot be exactly represented by any simple model, the quest here was to identify and apply a parsimonious hydrodynamic model that could provide useful approximations and be informative to the scientific community seeking a systematic understanding of the origin of the properties of colloidal gels.

The case studies discussed here have argued that dynamic simulations of attractive colloidal dispersions must include at a minimum long-ranged hydrodynamic interactions to recover real world observations. There are many fast simulation methods in the literature that can resolve the relevant fluid mechanics with similar fidelity as the ones employed here. However, dynamic simulations of colloidal gels in the absence of hydrodynamic interactions unambiguously provide inadequate comparison with experimental results, lead to significant inaccuracies when predicting the evolution of the microstructure and yield erroneous estimates of viscoelastic and mechanical properties in concentration regimes relevant to colloidal gels.
The structure of any arrested gel is a sensitive function of the hydrodynamic flows around diffusing particles and aggregates. Modeling the correct kinetics - by correctly accounting for hydrodynamic interactions - is fundamentally necessary for a computational scheme to match real world observations. In the study of the large discrepancies between Brownian Dynamics and simulations accounting for long-ranged hydrodynamic interactions, lubrication and higher order long-ranged hydrodynamic forces were intentionally neglected. Based on perturbation analysis, it was argued that lubrication merely softens the elastic response and induces a shift in the time scales of kinetic arrest, but does not influence the outcome of gel network growth. Indeed, a normal mode analysis has rigorously shown that hydrodynamic lubrication retards the relaxation rates, but ultimately does not affect the modes of relaxation of colloidal aggregates and entire network domains. Similarly, higher order moments of the hydrodynamic traction force do not appreciably alter the collective dynamics exhibited by a colloidal gel.

In an analogy to the Zimm model in polymer physics, long-ranged hydrodynamic interactions play a crucial role in determining the microscopic dynamics and macroscopic properties of colloidal gels. The response of, and the stress experienced by a network subject to external forces will also depend on the hydrodynamic flows through its pores and around particle rich regions. The dynamic simulations accounting for long-ranged hydrodynamic interactions employed here can quantitatively – for the first time in the published literature – describe nonlinear flow phenomena in sheared and sedimenting gels. The phenomenological models developed in this thesis aid in identifying regimes of intact gels and network breakdown as well as characterizing the onset and evolution of instabilities. By imposing a flow or external fields, material processing can change the cluster size and heterogeneity of the network and thereby alter the resulting gel mechanics. In fact, published work not included in this thesis has shown that predictions of this parsimonious model agree with experiments quantitatively in both the elastic modulus of the gel and the micro-structural correlation length. These results represent a fundamental step towards developing predictive computational capabilities for the engineering design of the structure and mechanical properties of colloidal gels.

Nonetheless, a minimal model can benefit from added layers of complexity, if the appended model proves to be even more illuminating and useful. A comprehensive comparative
study among BD, RPY and Stokesian Dynamics simulations to identify more subtle effects of hydrodynamic forces could be a worthwhile endeavor. This would provide a decisive assessment of the relative importance of the various hydrodynamic forces in the growth of gels, their mechanical properties and structural breakdown. The feasibility of such a study depends on the successful development of Fast Stokesian Dynamics, which would enable the simulations of colloidal gels on the same length and time scales as done in this thesis using BD and RPY simulations. Certainly, simulations employing lubrication and higher order hydrodynamic moments would enable a more accurate description of all contributions to the stress in a deforming gel and provide quantitatively accurate results for the viscosity and other rheological properties. The evolution of residual stress in the network and the role played by hydrodynamic interactions during gel aging are also of particular interest.

However, even more elucidating could be to study the effect of macroscopic boundaries in simulations. The question remains how the analysis is affected if conditions other than periodic boundaries are considered. For hard sphere colloidal dispersions it is well known that confinement introduces inherent hydrodynamic inhomogeneities and anisotropies and one wonders how these alter the dynamics of an attractive dispersion. It can be expected that the kinetics of gel growth, whether proceeding through cluster aggregation or spinodal decomposition, will remain unaffected by confinement as the process occurs in the bulk of the dispersion. In contrast, numerous experiments have now shown, that the dynamics of gel sedimentation, largely a pressure-driven flow down a channel, is highly sensitive to the conditions at the boundaries and interfaces. Consider further, that the results in chapters 7 and 8 show that the magnitude of the hydrodynamic forces at the boundary critically affect the phase map of stability of sheared colloidal gels. Even with the crude representation of walls employed in chapter 8 it was possible to successfully recover the experimentally observed log-rolling phenomena as a result of stagnation points in the flow field under confinement. More accurate hydrodynamic models of the flow fields near boundaries will most likely be necessary to study even more complex flow phenomena.

The interactions between the particles considered in the model colloidal dispersion might also be modified. This thesis has only used central forces between interacting particles and has thus not addressed the role of bond rigidity and its influence on the dynamic response.
of colloidal gels. Careful experimental measurements of colloidal bonds have however confirmed the existence of bending moments and have quantified their strength. Certainly, bond rigidity quantitatively affects the mechanisms of stress relaxation and models including it will yield even better predictions of the gel rheology. Accounting accurately for hydrodynamic torques and stresslets that enable more intricate collective dynamics will be critical for the outcome of these simulations. Already, computer simulations that model frictional contacts between neighboring particles and the relevant fluid mechanics have successfully extended our understanding of rheological phenomena such as discontinuous shear thickening and show promising predictive capabilities. More fundamentally, incorporating noncentral forces between bonded particles could open new avenues of investigation on the arrested state of gels. The isostaticity condition of Maxwell might not necessarily be an applicable criteria of gelation and structural arrest does not necessarily have to coincide with dynamic arrest anymore.

In terms of the shape of the colloids too, this work has employed a minimal model in considering only spherical particles with limited poly-dispersity. It is well known that highly eccentric particles or dispersions with large size disparities are described by significantly varying thermodynamic phase diagrams and behave dynamically different to mono-disperse spheres. While the analysis presented here is only considered to be a zeroth order approximation to these systems, it is reasonable to expect that accurate representations of hydrodynamic interactions will only be more important in models of disparately sized particles.

A future investigation will have to consider the stability of attractive colloidal dispersions after extensive deformation and their application to industrial processes remains an open question for future investigations. The formation and then break down of structure and the associated rheological properties of colloidal gels have been studied extensively in this work. However, the healing of these kinetically arrested structures and the restoration of visco-plastic properties such as the dynamic yield stress have not been investigated. What are the implications for the structural recovery, relaxation and residual stresses upon cessation of flow in these materials. Some thixotropic models for the rheology couple a constitutive expression for the stress in the material to a dynamic equation for a gross measure of the
material's microstructure. However, for colloidal gels, a microscopically observable order parameter characteristic of healing after deformation has been difficult to identify experimentally. Detailed simulations accounting for the hydrodynamic interactions could enable careful studies of aggregation kinetics, quantifying the birth-death rates of clusters. Then, modeling the evolution of population balances using probabilistic processes could offer one means of discovering the desired connection between microscopic degrees of freedom and macroscopic properties.

In conclusion, the original idea of this thesis lies in identifying the necessary minimal model of colloidal gelation based on sound physical reasoning. It has been demonstrated decisively how known and newly developed methods and simulation tools need to be employed to be useful for a range of modeling efforts with reliable predictive capabilities. Indeed, the main accomplishment of this research is the success in reproducing known experimental results and providing sound and simple phenomenological explanations for flow phenomena observed in a large variety of experimental systems and in numerous promising applications. The newly developed quantitative theories suggest a number of interesting possibilities for engineering the mechanical properties of colloidal gels. It is the hope that the findings discussed within this thesis have convinced the reader that an attempt to model colloidal gelation and the dynamics of kinetically arrested materials without accounting for long-ranged hydrodynamic interactions is futile. There is no doubt that the properties and mechanical response of these networks is fundamentally altered by the collective dynamics enabled by many-body hydrodynamics. While the work presented here only represents the first step in the right direction, the path to developing truly predictive computational models of colloidal gels is now laid out.
Appendix A

Measurement and Analysis of Parameters of Colloidal Dispersions

In what follows we give an overview of the various tools and methods that were applied in order to compute all relevant quantities for the results discussed in this thesis. All analysis, unless noted otherwise, was performed in MATLAB based on the particle level information provided by the dynamic simulations performed using Hoomd-blue. The relevant scripts along with their instructions can be found in the archives of the Swan research group.

A.1 Cluster size and nearest neighbor analysis

At any instant in time the particle positions can be extracted directly from the .xml files that Hoomd-blue outputs. As the number of particle in the simulations can grow very large, the easiest way to determine the number of nearest neighbors of each particle, as well as the size and distribution of distinct clusters, is by employing concepts from graph theory.

Unweighted, undirected graphs representing each cluster are constructed by associating every particle with a vertex and every bond between two particles with an edge connecting the corresponding vertices. The group’s CellList and NeighborList scripts are used to construct particle neighbor lists for every particle within a cutoff distance, \( r_{\text{cut}} \). Two particles are bonded if their separation is \( r \leq 2(1 + \delta) \). The resulting adjacency matrix \( A^c \in \mathbb{R}^{N \times N} \) encodes the topology of the interparticle bond network in a way that is abstracted from
the particles’ spatial arrangement. An entry of 1 for $A_{ij}^c$ indicates an existing connection between particles $i$ and $j$ and a value of 0 indicates no bond. $\sum_j A_{ij}^c$ is then equal to the number of neighbors of particle $i$, $N_c$, and the probability distribution over all particles is readily computed. The MATLAB function `graphconncomp(A_c)` identifies the connected components in the dispersion, and subsequently the clusters and the distribution of cluster sizes can be determined. In an attractive dispersion, the largest cluster is typically identified as the percolating gel network.

To detect percolation, i.e. if the largest cluster is connected to itself through periodic boundaries, the particle positions are replicated in each dimension for a fictitious simulation box with eight times the volume. The cluster analysis is repeated on this enlarged system. The network is said to be percolated or system-spanning, if there is still one unique largest cluster present that is eight times larger than in the original system. The gel is said to percolate along one or two dimensions, if the largest cluster is twice or four times the size respectively.

Once the particles belonging to a single cluster are identified, the squared radius of gyration tensor, $R_g^2$, of each cluster can be computed as defined for the case of log-rolling cylinders in (8.1). If the cluster is significantly anisotropic, the eigenvalues of $R_g$, $\lambda_g$, are the most informative. Alternatively, the scalar radius of gyration is given by the average over these eigenvalues.

### A.2 Calculation of static and dynamic structure factors

The static structure factor as defined in (3.1) is in fact equal to the Fourier transform of the real space number density fluctuations, $S(q) = \mathcal{F}(n - \langle n \rangle) \times \mathcal{F}(n - \langle n \rangle)^*/N$. Using the `fft` algorithm it is then possible to readily compute wave space correlations from simulations. However, as the particles in the dispersion are not distributed uniformly on a periodic grid, the Non-uniform Fast Fourier Transform algorithm of the first type, `nufft3dl` has to be employed [251] and the three-dimensional structure factor, $S(q_x, q_y, q_z)$, can be evaluated at a fixed instant in time. Alternatively, by correlating the density fluctuations in wave space over a specified lag time, the coherent scattering function is computed as: $F(q, t) =$
The incoherent scattering function can be evaluated for the same wave vectors as: 

\[ F_S(q, t) = \sin \left( q (x(t) - x(0)) \right) / q (x(t) - x(0)) / N. \]

Due to the finite size \( L \) of the simulation box, the maximum resolution in wave space is limited to \( q_{\text{min}} = dq = 2\pi / (L/2) \), and the wave vectors take on discrete values: \( q_x = q_y = q_z = -\pi/2 : dq : \pi/2 \). The isotropic structure factor is computed for wave vectors \( q = \sqrt{q_x^2 + q_y^2 + q_z^2} \), but a radially uniform sampling of \( S(q_x, q_y, q_z) \) is not possible. The two or one-dimensional structure factor can be found by only considering values of \( S(q_x, q_y, q_z) \) where the perpendicular wave vector(s) is(are) equal to zero, e.g. for the flow–vorticity plane we consider values \( S(q_x, 0, q_z) \). However, when a colloidal dispersion is sheared, the deformation of the simulation box means that the wave space lattice vectors are deformed accordingly and \( q_y^{\text{sheared}} = q_y - \gamma q_x \). This means, that \( q_y^{\text{sheared}} = 0 \) is not accessible for most values of \( \gamma \). The flow–vorticity plane can effectively only be sampled when there is zero strain on the simulation box. The results for \( S(q) \), \( F(q, t) \) and \( F_S(q, t) \) can be greatly improved by sampling from repeated simulations to reduce the amount of noise, especially for small samples. Often of interest, is the precise value of \( q_{\text{max}} \) at the peak value of the structure factor. This can be found by fitting a parabola or a Lorentzian-type function to interpolate around the observed peak of raw scattering result.

A.3 The box-counting dimension

The box-counting, or Minkowski-Bouligand dimension, is defined as [79]:

\[ d_f = \lim_{r_{cut} \to 0} \frac{\log (N(r_{cut}))}{\log (1/r_{cut})}. \]  

(A.1)

Here, \( N(r_{cut}) \) is the number of cubic boxes tessellating three dimensional space that are nonempty, i.e. cover the colloidal dispersion. Using the CellList and NeighborList scripts repeatedly to construct the neighbor lists with decreasing \( r_{cut} \) values and counting the number of tessellating cells that contain particles, it is possible to identify the power law relationship \( N(r_{cut}) \sim 1/r_{cut}^{d_f} \) for sufficiently small values of \( r_{cut} \), as illustrated in figure A-1.

The value of \( d_f \) obtained this way can be compared to the power law behavior of \( S(q) \).
Figure A-1: The number of boxes that contain particles as a function of inverse box size exhibits a power-law relationship (dashed lines) for fractal objects over length scales small compared to the system size, and depends on the gel structure determined among others by the network strength, $\epsilon = kT/U_A$. The power-law exponent is a direct measure of the fractal dimension, $d_f = 2.1, 2.2$ and $2.25$, respectively.

Beyond the large length scale correlation peak, $q > q_{\text{max}}$, it is expected that $S(q) \sim q^{-d_f}$ since the total correlation function scales as $g(r) - 1 \sim r^{1-3/d_f}$ [80].

### A.4 Estimation of empty pore volume

The evolution of empty pore volume in a gel, as done for collapsing freely settling gels in chapter 9 is computed using an approach similar to the box-counting method. At each point in time $t$ in the simulation the simulation box is tessellated into a three dimensional grid of cubic boxes of size $r_{\text{cut}}$. The density of particles in each box, $N_{\text{box}}$, is counted and the distribution of particle number densities, $P(N_{\text{box}})$, is computed (black line in figure A-2). For a nascent randomly percolated gel structure of fractal dimension $d_f$, this distribution should resemble a Gaussian with mean related to the bulk volume fraction $\phi$ and the width of the curve, its variance, will be a function of $d_f$, i.e. $P(N_{\text{box}})_{\text{gel}} \sim e^{-(N-f(\phi))^2/2\sigma(d_f)^2}$. In contrast,
the streamer is largely void of particles and thus $P(N_{\text{box}}^{\text{streamer}})$ increases monotonically as $N_{\text{box}} \to 0$. For any $t$, the observed distribution of $N_{\text{box}}$ will be the sum of these two distributions.

For each $t$, $P_{\text{gel}}$ is found by fitting a Gaussian to the observed distribution (black dashed line) and $P_{\text{streamer}} = P - P_{\text{gel}}$ can be computed (shown in red in the figures). The streamer volume is the total free volume in this fraction of boxes (area under the red curve) that do not cover the intact network but are inside the streamer. As the gel settles and the network evolves and as the streamer volume increases, the relative fraction of the area under these two curves will shift. Initially, the total volume of the empty pore space is below the threshold of accuracy of the method (blue dot-dashed line). Over time, $P_{\text{streamer}}$ increases as the streamer starts to expand. Close to $t_{\text{crossover}}^{\text{volume}}$, $P_{\text{streamer}}$ rapidly increases and the streamer volume exhibits a power-law growth. While the peak value of the Gaussian fit for $P_{\text{gel}}$ will decrease, its mean and variance should remain the same as long as the majority of the network is intact and only mildly compacts - as we indeed observe. At later times (not shown) after network integrity loss the method fails as now the simulation contains a random isotropic dispersion and an intact gel cannot be distinguished from the streamer.

A.5 Measurements of rheological quantities

Hoomd-blue computes the osmotic pressure tensor of the colloidal dispersion at every user defined instance. Care must be taken, as this means that the deviatoric stress components have the opposite sign than conventionally in the field of rheology.

Traditionally, mechanical spectroscopy of a materiel consists of performing SAOS with a discrete frequency sweep. The material is sequentially excited with a sine step of fixed frequency and the elastic and loss moduli are measured. To cover a large enough frequency spectrum, this approach requires a long measuring time in both simulations and experiments, often making it prohibitive to obtain the complex moduli of a material at all. While classical sine waves maintain a constant frequency at any point in time, chirp signals are designed so that their instantaneous frequency is continuously changing, hence they are also referred to as sine sweeps and enable the measurement of the system linear transfer function, i.e. the
Figure A-2: The distribution of particle number densities at $t = 0, 100, 300$ and $500\tau_D$ for a specific settling condition of: $\delta = 0.1$, $\epsilon = 0.05$, $G = 0.5$ and $\phi = 20\%$ (same gel as shown in figure 9-3). The densities shown are the overall distribution of $N_{box}$ in the entire simulation, the Gaussian fit approximating the density in the intact gel structure and the difference of these two, which constitutes the particle number density in the streamer. The detection threshold of the method is also indicated (blue dot-dashed line).
complex modulus of the material. Exponential chirps in particular maximize the signal-to-noise ratio and significantly reduce the overall measurement time. More details can be found in references [252–254].

In Hoomd-blue, using the chirp plugin developed in the group, any desired chirp signal, i.e. strain input $\gamma(t)$ can be applied to the material and the resulting $\sigma_{xy}(t)$ measured. The user only needs to specify the initial and final perturbation frequency of interest, $\omega_0$ and $\omega_f$, and the overall simulation time: $t = 2\pi/\omega_0$. The complex modulus of the simulated material is then given by the ratio of the Fourier transforms, computed in MATLAB, of the output and input signals:

$$G^*(\omega) = \frac{\mathcal{F}(\sigma_{xy})}{\mathcal{F}(\gamma)},$$

(A.2)

scaled appropriately on either $kT/a^3$ or $U_A/a^3$. The corresponding complex viscosity is calculated using the relationship: $\eta^*(\omega) = G^*(\omega)/\omega$. However, as the chirp signal is applied over a finite frequency domain, spectral leakage at the limits and ringing can occasionally be a problem and increase the noise of the measured data. Therefore, the original frequency-modulated, constant-amplitude chirp can be modified by using a particular cosine-tapered function, also called Tukey window with a single adjustable tapering parameter $r_T$, resulting in an optimally windowed chirp signal [254]. This enables more precise measurements, especially near $\omega_0$ and $\omega_f$. In the group, it has been found that a value of the tapering parameter of $r_T = 0.1$ provides the best results.

As discussed in chapter 6, the time dependent relaxation modulus is obtained by introducing a step-strain $\gamma_0$ in the simulation at $t = 0$. By measuring the subsequent shear stress $\sigma(t)_{xy}$, the relaxation modulus can be found from $G(t) = \sigma(t)_{xy}/\gamma_0$.

A.6 Computation of the density of states

The density of states for the normal mode analysis can be obtained from the eigenspectrum of the relevant matrix, either of $H$ or of $MH$. Since both $H \in \mathbb{R}^{3N \times 3N}$ and $M \in \mathbb{R}^{3N \times 3N}$, the computation time required for this analysis is currently prohibitive beyond $N = 10^4$ particles. Hoomd-blue is used to generate random particle configurations and to compute the associated $M$. The appropriate Hessian can be constructed in MATLAB and the $\text{eig}$ function.
used to find the list of eigenvalues $\lambda_i$ and associated eigenvectors $v_i$. The eigenvectors are made orthonormal by employing the lower triangular matrix of the Cholesky decomposition of the hydrodynamic mobility. The three lowest computed eigenvalues of the configuration correspond to the three degrees of translational freedom of the center of mass of the entire configuration and are therefore discarded from any subsequent analysis.

As the obtained eigenspectrum is not continuous, computing $P(\lambda)$ directly and finding the power law scaling of the DOS is challenging. Instead, first the relaxation spectrum is computed. This is the probability density function of the natural logarithm of the eigenvalues: $R(\lambda) = P(\log(\lambda)) = \lambda P(\lambda)$ as described in [131]. The discrete values of the relaxation spectrum are smoother and easier to bin so that $R(\lambda)$ can be reliably determined. A clear power law decay, $R(\lambda) \sim \lambda^{-\nu+1}$, can be identified and $P(\lambda)$ and $\nu$ readily computed.
Appendix B

Nomenclature

B.1 Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AHS</td>
<td>Adhesive Hard Spheres</td>
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<tr>
<td>ASD</td>
<td>Accelerated Stokesian Dynamics</td>
</tr>
<tr>
<td>BD</td>
<td>Brownian Dynamics</td>
</tr>
<tr>
<td>CPU</td>
<td>Central Processing Unit</td>
</tr>
<tr>
<td>DOS</td>
<td>Density Of States</td>
</tr>
<tr>
<td>FF</td>
<td>Far-Field</td>
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<tr>
<td>FLD</td>
<td>Fast Lubrication Dynamics</td>
</tr>
<tr>
<td>FPD</td>
<td>Fluid Particle Dynamics</td>
</tr>
<tr>
<td>FTS</td>
<td>Force-Torque-Stresslet</td>
</tr>
<tr>
<td>GPU</td>
<td>Graphical Processing Unit</td>
</tr>
<tr>
<td>HI</td>
<td>Hydrodynamic Interactions</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>MSD</td>
<td>Mean squared displacement</td>
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<tr>
<td>NF</td>
<td>Near-Field</td>
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<tr>
<td>NMA</td>
<td>Normal Mode Analysis</td>
</tr>
<tr>
<td>PSE</td>
<td>Positively-Split Ewald</td>
</tr>
<tr>
<td>RLCA</td>
<td>Reaction Limited Cluster Aggregation</td>
</tr>
<tr>
<td>RPY</td>
<td>Rotne-Prager-Yamakawa</td>
</tr>
</tbody>
</table>
SALR  Short-ranged Attraction and Long-ranged Repulsion
SALS  Small Angel Light Scattering
SANS  Small Angle Neutron Scattering
SAOS  Small Amplitude Oscillatory Shear
SD    Stokesian Dynamics

B.2 Dimensionless numbers

\( B_2^* \)  Reduced second virial coefficient
\( \hat{b} \)  Excluded annulus parameter
\( G \)  Gravitational Mason number
\( \text{Mn} \)  Mason number
\( \text{Mn}^* \)  Mason number scaled on most probable bond rupture force
\( \text{Mn}_c^* \)  Critical Mason number for fluidization under shear
\( \text{Mn}_H \)  Critical Mason number for shear-induced structuration under confinement
\( \text{Pe} \)  Péclet number
\( \text{Re} \)  Reynolds number
\( \text{Sc} \)  Schmidt number
\( \hat{U} \)  Interaction potential scaled on thermal energy
\( T_{\text{collapse}} \)  Stability criteria for collapse
\( T_{\text{process}} \)  Stability criteria during process duration
\( T_{\text{shelflife}} \)  Stability criteria during material lifetime
\( \hat{t} \)  Time normalized on Kramers escape time

\( \alpha \)  Oscillation frequency normalized on relative two-body diffusive time scale
\( \Delta \eta^* \)  Normalized complex viscosity difference
\( \delta \)  Attraction range normalized on particle radius
\( \epsilon \)  Network strength
\( \phi \)  Particle volume fraction
B.3 Parameters and variables

\( \mathbf{A}^{c} \) Graph adjacency matrix

\( A \) Yukawa parameter

\( A(N) \) System size dependent coefficient of structural breakdown under shear

\( A(r) \) Scalar hydrodynamic function of advection parallel to line of centers

\( A_{f}(q) \) Alignment factor

\( \hat{A}_{f}(q) \) Modified alignment factor

\( A_{xy} \) Aspect ratio of simulation box in the flow–flow gradient plane

\( a \) Particle radius

\( a_{i} \) Collision radius of aggregate of size \( i \)

\( B(r) \) Scalar hydrodynamic function of advection perpendicular to line of centers

\( b \) Hard sphere radius in excluded annulus model

\( C \) ratio of \( H \) to \( L_{g} \) representing lower threshold for validity of bulk measurements

\( \mathbf{D} \) Relative diffusivity tensor

\( D \) Stokes-Einstein diffusivity

\( D_{ij} \) Relative rate of aggregate diffusion

\( D_{R} \) Rotational diffusivity

\( d \) Spatial dimension

\( d_{a} \) Particle polydispersity around mean \( a \)

\( d_{f} \) Fractal dimension / Box counting dimension

\( d_{i} \) \( i \)th scalar constant

\( d_{xy} \) Characteristic size of log-rolling cylinder in the flow–flow gradient plane

\( \mathbf{E} \) Symmetric strain tensor

\( E \) Elastic modulus

\( \mathbf{F}^{B} \) Brownian force vector

\( \mathbf{F}^{G} \) Gravitational Force vector

\( \mathbf{F}^{H} \) Hydrodynamic force vector

\( \mathbf{F}^{P} \) Interparticle force vector

\( \mathcal{F}(i) \) Fourier transform of quantity \( i \)

\( F(q, t) \) Coherent scattering function
$F_S(q,t)$ Incoherent scattering function

$f(r)$ Perturbation function to $g(r)$

$\dot{j}$ Bond force loading rate

$\bar{j}$ Most probable bond rupture force

$G(r)$ Scalar hydrodynamic function of diffusivity parallel to line of centers

$G(t)$ Relaxation modulus

$G^*$ Complex modulus

$G_\infty$ Thermodynamic contribution to $G(t)$

$g$ Gravitational acceleration vector

$g$ Amplitude of gravitational acceleration

$g(r)$ Radial distribution function

$g^e(r)$ Equilibrium radial distribution function

$H$ Hessian of the interaction potential

$H_a$ Hydrodynamic advection tensor in shear flow

$\mathcal{H}(r)$ Heaviside function

$H$ Confining dimension under shear/Gap size

$H(r)$ Scalar hydrodynamic function of diffusivity perpendicular to line of centers

$h(t)$ Height profile of the gel

$h_0$ Initial height of gel

$I$ Identity tensor

$J$ Rate of particle motion at network/streamer interface

$j$ Flux of particles per unit area at network/streamer interface

$K$ Normalized rate of collision

$K(r)$ Scalar hydrodynamic function of stress generated in an extensional flow field

$K(i,j)$ Coagulation kernel of aggregates of size $i$ and $j$

$k$ Boltzmann constant

$k(l)$ Effective elastic spring constant over length scale $l$

$k_0$ Characteristic bond stiffness

$k_{\text{break}}$ Bond breaking rate

$L^H$ Hydrodynamic torque vector
$L$  Primary dimension of simulation box
$L(r)$  Scalar hydrodynamic function of stress generated in an extensional flow field
$L_{Ch}$  Channel dimension
$L_g$  Aggregate length scale
$l$  Characteristic length scale
$l_f$  Navier slip length
$\ell$  Exponent of normal mode dispersion relation
$\mathcal{M}$  Grand mobility tensor
$\textbf{M}$  Velocity-Force hydrodynamic mobility tensor
$\textbf{M}_{I,J}$  Hydrodynamic mobility tensor coupling velocity component $I$ to force moment $J$
$M(r)$  Scalar hydrodynamic function of stress generated in an extensional flow field
$m$  Particle mass
$N$  Number of particles
$N_{ag}$  Number of aggregates
$N_b$  Number of particle bonds
$N_{box}$  Number of particles in a cubic box of size $r_{cut}$
$N_c$  Number of particle contacts
$N_{Ch}$  Number of particles in channel
$N_L$  Number of cylinders in log-rolling dispersion
$N_g$  Number of particles in aggregate
$N_i$  Number of aggregates of size $i$
$N_s$  Number of solvent particles
$n$  Number density of particles in bulk
$\hat{n}$  Number surface density of particles
$n_i$  Number density of aggregates of size $i$
$P(i)$  Probability density function of random variable $i$
$p$  Pressure
$Q^{Ch}$  Volumetric flowrate through channel
$Q^D$  Volumetric flowrate through Darcy medium/gel
$q$  Wavevector

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$q$ Wavevector amplitude
$q_4$ $q$-type bond order parameter of order 4
$q_6$ $q$-type bond order parameter of order 6
$q_i$ Characteristic wavelength of mode $i$
$q_x$ Amplitude of wave vector in flow direction
$q_y$ Amplitude of wave vector in flow gradient direction
$q_z$ Amplitude of wave vector in vorticity direction
$q_{xy}$ Characteristic wavelength in flow–flow gradient plane
$q_{xz}$ Characteristic wavelength in flow–vorticity plane
$R$ Hydrodynamic resistance tensor
$R_g$ Radius of gyration tensor
$R(i)$ Probability density function of random variable $\log(i)$
$R(t)$ Radius of streamer
$R^*$ Characteristic radius of collapse
$R_0$ Initial radius of streamer at $t = 0$
$R_g$ Polymer radius of gyration
$r$ Center-to-center vector between particles
$\hat{r}$ Center-to-center unit vector
$r$ Distance between particle centers
$r_{cut}$ Cutoff distance
$r_{eq}$ Equilibrium particle distance
$r_i$ Residual in power law fit for mode $i$
$r_T$ Tukey tapering parameter
$S^B$ Brownian stresslet tensor
$S^H$ Hydrodynamic stresslet tensor
$S^P$ Interparticle stresslet tensor
$S(q)$ Static structure factor
$S_{\nu_i}(q)$ Structural correlation factor of mode $i$
$S_x(q)$ One-dimensional static structure factor along the flow direction
$S_y(q)$ One-dimensional static structure factor along the flow gradient direction
$S_z(q)$  One-dimensional static structure factor along the vorticity direction
$S_z(q)$  One-dimensional static structure factor along the vorticity direction
$s$  Standard deviation of sample
$T$  Solvent temperature
$t$  Time
$t_{\text{blowup}}$  Critical time point in exponential streamer growth
$t_{\text{crossover}}$  Time scale of transition to power law growth of settling rate
$t_{\text{volume crossover}}$  Onset of growth in streamer volume
$t_d$  Time scale of collapse process observed in experiments
$t_{\text{induction}}$  Nucleation time scale of velocity fluctuations
$t_{\text{poroelastic}}$  Time scale of poroelastic collapse
$t_{\text{shelflife}}$  Desirable lifetime of gel defined by use case
$U$  Translational particle velocity
$U_r$  Relative translational velocity between particles
$U(r)$  Pairwise interaction potential
$U_A$  Interaction strength at contact
$U_{AO}$  Asakura-Oosawa potential
$U_{HS}$  Hard sphere potential
$U_{\text{coex}}$  Interaction strength at point of coexistence
$U_{\text{crit}}$  Critical potential in linear viscoelastic response
$U_R$  Repulsive potential
$u$  Solvent velocity
$u$  Network settling velocity
$u_{\text{final}}$  Terminal settling velocity
$u_{f}^{ch}$  Fluid velocity through channel
$u_{f}^{D}$  Fluid velocity through Darcy medium/particulate network
$V(t)$  Streamer volume
$\mathbf{v}_i$  Eigenvector of particle displacements of normal mode $i$
$W(r)$  Scalar hydrodynamic function of diffusivity
$W_{ij}$  Collision efficiency

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$w$  Stretched coordinate in the boundary layer

$\dot{w}_4$  $w$-type bond order parameter of order 4

$\dot{w}_6$  $w$-type bond order parameter of order 6

$x(t)$  Particle configuration at time $t$

$x_{eq}$  Equilibrium particle configuration

$y$  Exponent of DOS

$z$  Elasticity exponent

$\alpha_0$  Relaxation rate of Maxwell mode

$\beta$  Exponent of stretched exponential

$\beta_C$  Exponent of coherent scattering function decay

$\beta_S$  Exponent of incoherent scattering function decay

$\dot{\Gamma}$  Strain rate amplitude tensor

$\Gamma$  Maximum strain rate

$\gamma$  Strain

$\dot{\gamma}$  Strain rate

$\gamma_0$  Amplitude of step-strain

$\varsigma$  Viscous drag coefficient

$\eta$  Dispersion viscosity

$\langle \Delta r(t)^2 \rangle$  Particle mean squared displacement

$\Delta t$  Time step of integration

$\Delta x$  Particle displacement

$\Delta \rho$  Density difference between particles and solvent

$\delta(t)$  Fluctuations around equilibrium configuration

$\delta(t)$  Dirac delta

$\eta^*$  Complex viscosity

$\eta_{HS}^*$  Hard sphere complex viscosity

$\eta_{Escape}^*$  Complex viscosity difference between attractive and hard sphere dispersions

$\eta'$  Real component of complex viscosity

$\eta''$  Imaginary component of complex viscosity

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$\eta_0$ Zero shear viscosity

$\eta_s$ Solvent viscosity

$\eta_\infty$ Infinite shear viscosity / Hydrodynamic contribution to dispersion viscosity

$\theta$ Polar angle

$\kappa$ Permeability of gel

$\kappa_D$ Inverse Debye length

$\kappa_i$ Collectivity index of mode $i$

$\Lambda$ Lacunarity (aggregate shape factor)

$\lambda_g$ Eigenvalue vector of radius of gyration tensor

$\lambda_0$ Wavelength of initially imposed density fluctuations in simulations

$\lambda_i$ Relaxation rate of normal mode $i$

$\lambda_f$ Inverse Navier’s slip length

$\lambda_s$ Steady-state wavelength of log-rolling structures

$\lambda_x$ Characteristic wavelength of log-rolling structures

$\mu_i$ Relaxation time of spring between surfaces corresponding to mode $i$

$\nu_i$ Normalization constant for $\kappa_i$

$\xi_{eq}$ Equilibrium surface-to-surface separation

$\Xi_{ij}$ Ratio of collision radii $a_i$ and $a_j$

$\rho$ Solvent density

$\Sigma$ Deviatoric stress tensor

$\sigma$ Surface tension

$\sigma_{xy}$ Shear stress in the flow–flow gradient direction

$\sigma_Y$ Yield stress

$\tau$ Wall shear stress

$\tau_D$ Time scale of particle diffusion

$\tau_G$ Time scale of particle settling

$\tau_T$ Time scale of particle momentum relaxation

$\tau_K$ Kramers escape time

$\tau_q$ Characteristic relaxation time scale

$\tau_{ve}$ Viscoelastic relaxation time
\( \Omega \)  Angular particle velocity

\( \omega \)  Small strain rate amplitude oscillatory shear frequency

\( \omega_0 \)  Initial frequency of chirp signal

\( \omega_f \)  Final frequency of chirp signal

\( \omega_i \)  Characteristic frequency of vibrations of normal mode \( i \)
Bibliography


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