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Phase Behavior and Rheology of Colloids with Polymer-Mediated Attractions

A Dissertation

Presented to

the Faculty of the Department of Chemical and Biomolecular Engineering

University of Houston

In Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in Chemical Engineering

by

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May 2019

Phase Behavior and Rheology of Colloids with Polymer-Mediated Attractions

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"I will thank you forever, because you have done it. I will wait for your name, for it is good, in the presence of the godly." Psalm 52:9

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Abstract

Mixtures of colloids and polymers are used in many industrial and commercial applications such as paints, consumer products, and drilling fluids. Addition of polymers to colloidal suspensions can cause attractions between the particles, such as depletion and bridging attractions. These attractions produce complex phase behavior and rheology of the final suspension. In addition to the attractions that arise, the properties of the polymer additives themselves – size, dispersity, charge/interaction with particle – likely also affect the final suspension behavior. In this work, we investigated the effects of these properties of the polymer additives to the phase behavior and rheology of the resulting suspensions. First, we explored the effect of polymer dispersity on the phase behavior of depletion mixtures by using unary and binary mixtures of uniform, small polymers as the depletant in a model colloidal suspension. We found that the phase behavior could be mostly collapsed, irrespective of polymer dispersity, if the polymer concentration was represented as a weighted sum of the two polymers' concentrations in a binary mixture. Then, a new model depletion mixture was developed for measuring stress-dependent rheological properties: shear thickening and first normal stress difference N_1 . Using this system, we measured the effects of polymer depletant size and dispersity on the rheology of a shear-thickening suspension. The presence of large polymers enhanced the shear thickening of the suspensions and changed the sign of N_1 from negative to positive, compared to the nearly hard-sphere suspension. Finally, we explored the effect of polymer adsorption strength on the surface of the particles on the cluster formation and rheology of a model bridging mixture, based on the same model colloidal suspension as the depletion studies. This bridging mixture is a promising model system for future systematic comparisons of the effects of depletion and bridging attractions. The results of this work confirm the importance of studying the effects of the properties of the polymer additives themselves on the final behavior of model colloids with polymer-mediated attractions, and they suggest that this understanding can be used to tune properties of the resulting suspensions.

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Chapter 1: Introduction

With particles of size ranging between $\mathcal{O}(10 \text{ nm})$ to $\mathcal{O}(1 \ \mu\text{m})$, colloidal suspensions experience thermal energy,^{1,2} and understanding the interactions between the particles are imperative to understanding the phase behavior and rheology of such suspensions. One of the most basic interactions between particles is the hard-sphere interaction,^{2,3} which is an infinite repulsion at contact without interaction at other separations. Experimentally, hard-sphere interactions are only approached by minimizing the intrinsic softness of interactions.³ Two ubiquitous interactions in colloidal suspensions are the electrostatic repulsion and van der Waals attractions, the sum of which can predict the stability of colloids (Derjaguin, Landau, Verwey, Overbeek – DLVO – theory).^{4,5} The range of the electrostatic repulsion is minimized by screening with added salts; van der Waals attractions are minimized by refractive index matching the solvent and particles and/or adding steric stabilizers.³ Once hard-sphere interactions are approached, other interactions can be systematically added to the suspensions to measure the effects of such interactions on quantities of interest.

1.1 Mixtures of colloid and polymer

One method of systematically adding forces between particles is the addition of macromolecules, such as polymers. Understanding polymer-induced interactions between particles is especially important because of the complex interactions that arise and because such mixtures (and more complex mixtures) are used in applications like paints, consumer products, and drilling fluids. The type of interaction that arises depends on many factors such as the relative concentrations and sizes of each species and whether the polymer adsorbs on the surface of the particles.^{6–8}

In this work, we focused on the addition of polymers (radius of gyration, R_g) that are significantly smaller than the particles (particle radius, a; $R_g/a < 0.1$) to induce attractive interactions.

1.1.1 Depletion attractions

If the polymer does not adsorb on the surface of the particles, an attraction known as depletion attractions arise.^{9,10} Because the polymer does not adsorb on the surface of the particles, each particle is surrounded by a layer excluded of the center-of-mass of the polymer. Then, as the particles move closer together, the polymers become "depleted" from the area between the surfaces of the particles, and the osmotic pressure from the imbalance of the polymer concentration between this area and the bulk solution pushes the particles together. Then, the range and strength of this attraction is controlled systematically by the size and concentration of the polymer additives.

The phase behavior of model depletion mixtures have been studied extensively both theoretically and experimentally. The phase behavior depends on both the strength of attraction and particle volume fraction, but also on the range of attractions.^{11,12} Experimentally, depletion attractions lead to cluster-formation at low particle volume fractions and gelation (interconnected network) at high enough concentrations of particles and polymers.^{12–16} This gelation arises from an arrested spinodal decomposition for short-ranged attractions ($R_g/a < 0.05$),^{15,17} and as such, the shape of the equilibrium phase diagram and the nonequilibrium gelation phase diagram take on very similar shapes.^{1,12}

The rheology of these model suspensions show a shear-thinning to yielding behavior with increasing polymer concentration, and thus increasing attraction strength.^{18–20} The yielding has been observed to be multi-step with possible explanations of such behavior being related to the multi-scale nature of such gels.^{21–23} There are many complexities in the relationship between the microstructure, inter-

actions, and the rheology that are the subject of active study (see special issue of J. Rheol.²⁴). The increase in low-shear viscosity due to yielding has been observed to obscure shear-thickening in dense suspensions with depletion attractions¹⁸ and other types of attractions.²⁵

1.1.2 Bridging attractions

If the polymer adsorbs on the surface of the particles, the excluded volume no longer exists around the surface of the particles, and thus depletion attractions no longer arise. However, when the polymer adsorption is strong enough, it can cause another type of attraction known as bridging attractions (see review Ref. 26). In this case, the polymer forms a physical bridge between the surfaces of the particles as it binds on multiple particles simultaneously. This type of attraction has been heavily utilized for flocculation in separation processes, such as treatment of waste water,²⁷ and so the mechanisms of polymer adsorption and flocculation/phase separation has been well studied and reviewed.^{26,28–32}

The phase behavior resulting from this type of attraction is still under investigation, especially in comparison to depletion attractions.^{33–35} There is a nonmonotonic dependence of polymer concentration on the attraction strength between particles in these systems. As the polymer concentration increases, initially, the attraction strength increases because of increasing bridges between the particles. Then, the attraction strength decreases upon further increasing the polymer concentration, because the surfaces of the particles become saturated with the polymer. Then, the polymer acts as a steric stabilizer, making the particles repulsive.³⁶ If the polymer concentration is increased further, depletion attractions can be recovered.³⁷ This type of behavior leads to a equilibrium reentrant phase diagram with increasing polymer concentration.³³ For the nonequilibrium gelation of the bridging mixtures, the mechanism is driven by kinetic arrest (percolation) rather than the arrested phase separation observed with depletion attractions.³⁵ Suspensions that exhibit bridging attractions have a wide variety of rheological signatures that result from the mechanism of bridging, as well. For instance, shear-induced bridging and reversible bridging, which is observed when the adsorption of polymers on the surface is weak, gives rise to shear thickening at high shear rates.^{38,39} Bridging attractions can give rise to shear thinning and yielding from the strong attractions between the particles and the formation of a gel network.⁴⁰ As such, the wide range of rheological behaviors depends on the sizes of the polymer and particle, concentrations of the polymer and particle, and the adsorption strength between the two species.

1.2 Objective and organization of dissertation

While model depletion and bridging suspensions have been well studied in terms of phase behavior and rheology, the effects of the real properties of the polymer additive on such systems have not been as thoroughly investigated (see 2.1, 4.1, 5.1). In many cases, the polymer additive is only thought of as the source of attraction, but the polymers themselves can have a significant effect on the phase behavior^{41–43} and rheology^{44,45} of such systems. In this work, we wanted to understand the effects of the properties of the polymers – the size, dispersity, and charge/interactions – on the phase behavior and rheology of suspensions with polymer-mediated attractions.

First, we investigated the effect of the polymer dispersity on the gelation phase behavior of the model colloidal suspension using unary or binary mixtures of two uniform polymers (Ch. 2). We discuss the collapse of the phase behavior across different polymer dispersities and the exceptions to this collapse. This study emphasized the importance of accounting for each size of polymers in a disperse mixture for predicting the phase behavior of suspensions with depletion attractions.

Next, we developed a model depletion mixture in a glycerol-water solvent for confocal microscopy and rheology (Ch. 3). The particles were refractive index- and

density-matched to the solvent for confocal microscopy, and the background viscosity was high enough to measure the stress-dependent rheological parameters: shear thickening and the first normal stress difference N_1 .

Then, using the new model depletion mixture, we investigated the effect of polymer size and dispersity on the shear thickening of attractive suspensions (Ch. 4). In the presence of large polymer (disperse or uniform), we measured an enhanced shear thickening and a change in sign of N_1 from negative (for nearly hard-sphere suspensions) to positive. We discuss the underlying mechanism of this change.

Finally, we studied the effect of polymer charge/adsorption strength on the surface of the particles on the cluster formation and rheology of a model bridging mixture (Ch. 5). We discuss the mechanism of adsorption, which was pH-tunable, and the relationship among the adsorption strength, size of clusters, and the re-sulting viscosity.

Chapter 6 gives the summary of this work and the open questions for future inquiry.

Chapter 2: Phase behavior of colloid-polymer depletion mixtures with unary or binary depletants

This chapter was published in *Soft Matter* with an accompanying correction.

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Park, N.; Conrad, J. C. Correction: Phase behavior of colloid-polymer depletion mixtures with unary or binary depletants. *Soft Matter* **2017**, *13*, 5085-5086.

To incorporate the supporting material into the chapter and for dissertation consistency, the numbers of references, figures, and tables were changed. The captions were shortened for the dissertation.

2.1 Introduction

Non-adsorbing macromolecules or nanoparticles induce attractive depletion interactions between microscale particles. Because both the strength and range of the attraction are readily tuned by the concentration and size of depletant, respectively, ^{9–11,46} mixtures of colloidal particles and depletants are commonly used to develop fundamental understanding of the effect of attractions on glass, ^{47,48} crystal, ^{49,50} and other phase transitions. ^{11,12,14,16,51,52} In industrial applications, depletion interactions induced by polymers added in storage or preparation may generate either desired structures⁵³ or deleterious aggregation ⁵⁴ in products. In biology, crowding within cells affects the diffusion of macromolecules, and thereby alters reaction dynamics, macrostructure assembly, and protein folding. ^{55–58} Recent studies suggest that depletion interactions arising from small crowders may be one of the factors affecting intracellular diffusion. ^{59,60} In each of these settings, dispersity in the size of depletants changes the range and strength of the attraction,

thereby altering the phase behavior of mixtures, the stability of industrial products, or the diffusion of macromolecules within cells. Hence fundamental understanding of the effects of depletant size dispersity is expected to provide insight into and improve control over a range of industrial and biological processes.

Mixtures of uniformly disperse colloids and polymers are widely used to study equilibrium and non-equilibrium phase behavior in theory and experiment. For example, earlier theoretical studies found that adding short-ranged attractions to suspensions of particles with hard-sphere repulsions expanded the region of fluidcrystal coexistence, whereas adding longer-ranged attractions resulted in fluidfluid phase separation.^{11,51} In addition to these equilibrium phase transitions, experimental studies of depletion mixtures identified a variety of non-equilibrium phases, including clusters, gels, and glasses.^{12–16,52} Most existing studies of phase behavior in depletion mixtures treated both particle and depletant as uniformly dispersed in size. Studies using theory/simulation⁶¹⁻⁶⁴ and experiment^{61,65-68} probing the effects of particle size dispersity reported appearance of new phases or shifts in the phase boundaries with concomitant fractionation of particles by size. Although fewer in number, the extant studies exploring depletant size dispersity also tantalizingly hint at significant changes in the phase behavior of depletion mixtures. As one example, the concentration of polymer required to induce flocculation experimentally shifted by an order of magnitude from theoretical expectations when polymers with large dispersity were employed as the depletant.^{69,70}

Systematic studies on the effect of depletant dispersity, however, report widely varying effects and hence are inconclusive. Theory and simulation studies, in which dispersity is readily tuned, have reported that increasing the dispersity of depletants: (1) increased both the range and strength of the attraction,^{71,72} thereby lowering the concentration of depletant needed for phase separation;^{41,73} (2) decreased the strength of attraction for constant depletant volume fraction;^{74,75} or (3)

negligibly affected the strength and range of depletion attractions.^{76,77} Similarly, contrasting experimental results suggest that the effects of polymer dispersity on interactions and phase behavior remain incompletely understood. Direct measurements of the force between a particle and a flat surface in a disperse polymer solution, for example, suggested that the smaller polymer in a mixture dominated the range of interaction,⁷⁸ or that knowledge of the whole distribution of polymer size was required to predict the attraction.⁷⁹ Likewise, contrasting effects of polymer size dispersity on non-equilibrium flocculation and gelation have been reported. Experiments using binary mixtures of polymers as depletant indicated that either the larger or smaller polymer could dominate flocculation, depending on the order in which polymers were added.⁴² Later experimental studies^{43,80} of gelation and flocculation, however, concluded that the larger polymer in mixtures controlled the phase behavior. Thus, understanding of the effects of polymer dispersity on non-equilibrium phase behavior remains limited and is the focus of this study.

Here, we show that the phase behavior of suspensions of charged colloidal particles containing dilute or semi-dilute unary or binary mixtures of polymer can be superimposed on a single phase diagram using an effective polymer concentration, $C_{p,N}$ (the sum of the individual concentrations of polymers in a mixture, each normalized by their respective overlap concentrations). We varied the size of the polymer over one order of magnitude and characterized the structure and dynamics of the resulting colloid-polymer mixtures using confocal microscopy. Structural and dynamic metrics were nearly independent of depletant size or dispersity when the concentration of the polymer mixture was represented as a sum of normalized concentrations of each species, suggesting that the phase behavior in a mixture of polymers of different sizes can be predicted from the phase behavior of uniformly disperse polymers; disparities in these metrics occurred only near the transition between distinct phases. The normalized polymer concentration, $C_{p,N}$, was better able to collapse the phase behavior than the correlation length even in the semidilute regime of the polymer, indicating that both sizes of polymer contributed to the effective interparticle interaction.

2.2 Materials and methods

2.2.1 Sample preparation

Suspensions of poly(methyl methacrylate) particles (PMMA) were prepared at volume fractions of $\phi = 0.05 - 0.45$ with various concentrations and sizes of polystyrene (PS) polymers as depletants. We synthesized sterically stabilized PMMA particles following established protocols.^{81,82} The average hydrodynamic radius of the particles was 990 nm and their polydispersity was 9%, as determined using dynamic light scattering. For imaging with the confocal microscope, particles were fluorescently labeled with Rhodamine B (Sigma Aldrich)⁸³ and dried for storage.

Each 0.5 mL sample was prepared by gravimetrically mixing pure solvent with stock suspensions/solutions of each component (particles, PS, and salt) in the solvent. The solvent was a mixture of cyclohexyl bromide (83.5 (w/w)%) and decahydronaphthalene (16.5 (w/w)%), formulated to nearly match the refractive index and density of the particles. To prepare samples with particle volume fractions $\phi \lesssim 0.25$, a $\phi = 0.48$ PMMA stock was diluted into each sample; to prepare samples with particle volume fractions $\phi \gtrsim 0.25$, dry PMMA particles were added directly to samples. We verified that both methods led to similar particle structure and dynamics by comparing the resulting radial distribution function and mean squared displacements for representative samples. A stock tetrabutyl-(ammonium chloride) salt (TBAC) solution was added to each sample to a final concentration of 1.5 mM to partially screen charges on the particles.^{84,85} The final TBAC concentration in solution — approximately 5 μ M — was much lower than the added con-

centration, due to the low degree of dissociation and solubility of TBAC in these solvent mixtures.⁸⁴ Stock solutions of two different PS polymers were prepared; the molecular weight (M_w , reported by the manufacturer) and radius of gyration (R_g , calculated from the measured intrinsic viscosity) of each polymer are given in Table 2.1. To vary the depletant dispersity and the attraction strength and range, we added one or two of the PS stock solutions to each sample. All PS used for this study induced short-ranged attractions, with $R_g/a < 0.05$, and the final concentration of PS in the free volume^{11,12} was calculated using a concentration-dependent depletion layer thickness.¹⁰

Table 2.1: Summary of molecular weight (M_w) and radius of gyration (R_g) of the polystyrene polymers used in this study. The values of M_w and M_w/M_n are obtained from the vendor; the radius of gyration R_g was determined from intrinsic viscosity measurements.

M_w [Da]	M_w/M_n	Vendor	R_g [nm]
6400	1.05	Scientific Polymers	2.8 ± 0.1
328,900	1.02	Agilent	23 ± 1

Vials containing all components of a desired sample were tumbled and rolled to thoroughly mix the contents, and left on the roller until imaging. Most experiments were performed within 10 days of sample preparation, but all samples were imaged within 29 days of preparation. We verified that the dynamics and structure did not change with sample age over this period by comparing images acquired of samples past 10 days from preparation to those acquired at an earlier time point.

2.2.2 Viscosity of PS solutions

We measured the viscosity of PS solutions at 20°C using a Discovery Hybrid Rheometer (DHR-2, TA Instruments) and a Couette geometry with bob length of 42 mm. The viscosity at 10 s⁻¹ for solutions at various C_p/C_p^* and M_w of PS collapsed onto a single curve with a quadratic dependence of viscosity on C_p/C_p^* and the yintercept fixed at the solvent viscosity (Fig. 2.1). Explicitly, we determined C_p^* for each of our samples by measuring the intrinsic viscosity and applying the relation $C_p^*[\eta] \sim 1$. The quadratic fit to the data, $\eta = \eta_s + 1.88c[\eta] + 1.39c^2[\eta]^2$, agrees with the Huggins equation within fitting errors. This quadratic fit to the data was used to estimate the background viscosity for each sample.



Figure 2.1: Viscosity of polystyrene solutions in mixture of decahydronaphthalene and cylohexyl bromide. The quadratic fit to the curve, $\eta = 2.36 + 1.88C_{p,N} + 1.39C_{p,N'}^2$ resulted in $R^2 = 0.96$ with a y-intercept of 2.36 mPa·s, which was the viscosity of the pure solvent.

2.2.3 Imaging and tracking of particles

Approximately 100 μ L of each sample was sealed in a chamber fabricated from glass cover slides using UV-curable adhesive (Norland Optical). We imaged samples using a point-scanning confocal microscope, VT Eye (Visitech, Sunderland, U.K.) that was connected to an inverted microscope (Leica DMI 4000, Leica Microsystems, Buffalo Grove, IL) equipped with a 63x (N.A. 1.4) oil-immersion objective. Imaging began approximately 30 minutes after each sample was loaded into its chamber. To capture 3-D *z*-stacks of images, we rapidly acquired 2-D images (at 18.6 frames per second (fps), 7.1 pixels/ μ m) that were spaced vertically by $\Delta z = 0.1 \ \mu$ m at heights from $z = 25 \ \mu$ m to 65 μ m above the bottom coverslip. To generate sufficient statistics for quantitative structural measurements, at least

nine z-stacks were acquired for $\phi = 0.05$ samples and at least three z-stacks were acquired for $\phi = 0.15$ samples; at higher volume fractions (i.e. for $\phi \gtrsim 0.25$), one or two z-stacks were acquired for each sample. To characterize the dynamics of the particles, 2-D time series of images were captured at approximately 11 fps (6.3 pixels/ μ m) at a depth of 30 μ m above the bottom coverslip.

We located the centers of the particles in 3-D in each z-stack using algorithms written in IDL.⁸⁶ The resolution of the particle centers was about 40 nm in the x-y plane and about 200 nm in *z*, as determined from the mean-squared displacement (MSD) of stationary particles. We removed from the analysis any particles that were within about 4 μ m of the edge in the x-y plane and within 1 μ m from the top and bottom. From the positions of the particle centers, we calculated the 3-D radial distribution function $g(r) = n(r)/(\rho 4\pi r^2 dr)$, where *r* is the distance from the center of particle, *dr* is the bin size, *n* is the number of particles in the shell between *r* and *r* + *dr*, and ρ is the bulk density of particles.

Using algorithms written in MATLAB, we located particle centers in 2-D in the time series of images and then tracked the particles over time.⁸⁷ To characterize the particle dynamics, we calculated the ensemble-averaged MSD, corrected for linear drift in the particle positions as $MSD = \langle (x(t+\tau)-x(t))^2 \rangle$, where *x* is the position of the particle, *t* is instantaneous time, τ is the delay time, and the brackets represent averages over ensemble and time.

2.3 Results and discussion

2.3.1 Signatures of polymer-induced structure and dynamics

We first examined metrics for the structure and dynamics of the PMMA particles in the absence of polymer-mediated attractions. While PMMA particles are often used to model hard spheres, they may become charged during synthesis, when suspended in cyclohexyl bromide solvent, or with addition of salt.^{84,85} In our experiments, the structure of the PMMA particles in suspensions without added depletant indicated that the particles were charged. The radial distribution function g(r) for the $\phi = 0.05$ suspension increased sharply at a separation corresponding to the particle diameter (r/2a = 1) but the first peak was shifted to r/2a = 1.7, indicating that particles exhibited long-range repulsive interactions (Fig. 2.2). Furthermore, the position of the first maximum of g(r), one measure of the average separation between particles, shifted to lower values as the particle volume fraction ϕ was increased from 0.25 to 0.45, as expected for suspensions of charged particles. The samples did not crystallize because the polydispersity of our particles was at or above the values where crystallization is observed.^{3,88,89}



Figure 2.2: Radial distribution function g(r) as a function of normalized radial distance r/2a for suspensions of PMMA without added polymer. The dashed line indicates the limiting value of g(r) at large r(g(r) = 1).

To estimate the electrostatic interactions between the PMMA particles, we measured the radial distribution function g(r) of a low-volume-fraction sample at $\phi \approx 0.01$ with approximately 1.5 mM TBAC, but without added PS. Sixty *z*-stacks were captured and analyzed as described in Sec. 2.2. The g(r) data at this low volume fraction was translated to the pairwise interaction potential between the particles via $\lim_{\phi \to 0} g(r) = \exp(-u(r)/k_BT)$.^{3,90} The screened Coulomb potential $\frac{u(r)}{k_BT} = \frac{a^2}{\lambda_B} \left(\frac{e\zeta}{k_BT}\right)^2 \frac{\exp(-\kappa(r-2a))}{r}$ was fit to the u(r) data, and the resulting fit was

translated back to g(r) for comparison with the experimental data (Fig. 2.3). The fit gave estimates for zeta potential (ζ) of -4.4 mV and for Debye length (κ^{-1}) of 480 nm. Using the estimated u(r) from g(r), we also calculated an effective hard sphere diameter: $d = 2a + \int_{2a}^{\sigma} [1 - \exp(-u(r)/k_BT)] dr$,^{8,92,93} where *d* is the effective hard sphere diameter, *a* is the particle radius, and σ is the radial distance at which u(r) = 0. We numerically integrated the u(r) data using the trapezoidal rule to calculate the effective diameter: d = 2300 nm. This diameter was 16% larger than the diameter measured using DLS.



Figure 2.3: The radial distribution function g(r) of a $\phi \approx 0.01$ PMMA suspension without added PS as a function of normalized radial distance (r/(2a)). The symbols are the data, and the dashed line is the screened Coulomb equation fitted to the data.

Likewise, changes in dynamics with ϕ as quantified by the ensemble-averaged one-dimensional MSD also indicated that the particles were charged. At $\phi = 0.05$, the MSD scaled with lag time as a power-law with exponent 1, i.e. MSD ~ τ^1 , consistent with Brownian diffusion; the experimentally-determined MSD closely agreed with that predicted from the Stokes-Einstein equation for a particle of the same size suspended in the same background viscosity as our samples (solid line in Fig. 2.4). The slight variation from the Stokes-Einstein estimate, $D_{SE} = k_B T/(6\pi\eta a)$, at short times was quantitatively accounted for by hydrodynamic interactions,

which reduce the self-diffusion coefficient to $D(\phi) \approx 0.92D_{SE}$ at this ϕ .⁹⁴ At volume fractions $\phi \ge 0.25$, however, the MSD was nearly constant at long lag times. The plateau in MSD signals caging of the particles by neighbors,^{95–97} and is usually expected at significantly higher volume fractions in hard spheres. Hence this result suggested that the effective volume fraction in our suspensions was higher than the actual particle volume fraction due to the long-range electrostatic repulsions between particles. As the volume fraction was further increased above $\phi = 0.25$ the height of the plateau decreased, suggesting that the particles were increasingly caged. The MSDs measured at the two highest ϕ were equal, indicating that the average cage size did not significantly change at these higher volume fractions. The cage size estimated from the limiting plateau MSD value, 140 nm, was of the same order of magnitude as the estimated Debye length (480 nm), consistent with strong caging due to the electrostatic repulsions.



Figure 2.4: Normalized mean-squared displacement $MSD/(2a)^2$ as a function of delay time τ for PMMA suspensions with no added polymer. The solid line indicates the MSD calculated from the Stokes-Einstein equation. The dashed line indicates the resolution of the tracking algorithm.

Adding PS polymers to induce attractions between the PMMA particles led to changes in both the structure and dynamics of the particles. We first examined the behavior of samples with added polymers of uniform molecular weight (328.9 kDa) as a function of depletant concentration and particle volume fraction. As PS concentration increased, the height of the g(r) maximum corresponding to the average interparticle separation decreased; concomitantly, a new local maximum appeared at a lower separation corresponding to the average particle diameter (r/2a = 1) (Fig. 2.5a-c). (The dashed lines in (a-c) indicate the limiting value of g(r) at large r.) The finite width of this contact peak nearly quantitatively reflected both the particle size dispersity and errors in locating the centers of particles. The appearance of the contact peak and its increase in height with PS concentration indicated that a significant fraction of particles was in near-contact with their neighbors, consistent with the formation of multiparticle structures such as clusters or gels.



Figure 2.5: (a-c) Radial distribution function g(r) as a function of r/2a and (d-f) MSD/ $(2a)^2$ as a function of non-dimensionalized delay time $\tau D/a^2$, for PMMA suspensions with 328.9 kDa PS. (d inset) MSD/ $(2a)^2$ as a function of delay time τ for suspensions with volume fraction $\phi \approx 0.05$.

Similarly, the dynamics of the particles also evolved with increasing PS concentration (Fig. 2.5d-f). (The dashed lines in (d-f) indicate the resolution of the measurement $\epsilon^2/(2a)^2$.) Increasing the PS concentration strengthened the depletion attraction but also increased the background solvent viscosity; both factors caused the diffusivity to decrease. To isolate the change in the MSD due to attractive interactions, the delay time was non-dimensionalized using the ratio of the Stokes-Einstein diffusion coefficient to the square of the radius of the particles, D/a^2 . This non-dimensionalization shifted the MSD of samples with added polymers to lower delay times. At the lowest particle volume fraction ($\phi = 0.05$), the MSD curves acquired at various concentrations of PS collapsed onto a single curve as a function of the viscosity-corrected delay time (Fig. 2.5d), indicating that the slowing of dynamics (Fig. 2.5d inset) was solely due to the increase in viscosity. We did not observe dynamics indicative of a depletion layer,^{98–100} likely because the range of depletion was less than 5% of the particle size in all samples. At higher particle volume fractions (e.g. $\phi = 0.25, 0.45$), the MSD decreased with increasing PS concentration at a fixed non-dimensional lag time (Fig. 2.5e,f); these changes indicated that the dynamics slowed due to the increase in the strength of the attractive interactions between particles. At $\phi = 0.45$, the magnitude of the MSD for samples with the highest concentrations of polymer was approximately equal to the tracking resolution $\epsilon^2/(2a)^2$, indicating that the particles were effectively arrested over the duration of the experiments. (Similar g(r) and MSD data for samples with only the lower molecular weight PS (6.4 kDa) are shown in Fig. 2.6. The dashed lines in (a-c) indicate the limiting value of g(r) at large r(g(r) = 1); the dashed lines in (d-f) indicate the resolution of the tracking algorithm $e^2/(2a)^2$.)

To investigate the effect of depletant dispersity on structure and dynamics, we examined g(r) and MSD for PMMA suspensions containing PS of two different sizes (Fig. 2.7, 6.40 kDa and 328.9 kDa). (The dashed lines in (a-c) indicate the limiting value of g(r) at large r; the dashed lines in (d-f) indicate the resolution of the tracking algorithm $\epsilon^2/(2a)^2$.) Like suspensions with depletants of uniform size,



Figure 2.6: (a-c) Radial distribution function g(r) as a function of r/2a. (d-f) Normalized mean squared displacement MSD/ $(2a)^2$ as a function of nondimensional delay time $\tau D/a^2$ for PMMA suspensions with 6.40 kDa PS.

at sufficiently high total PS concentration g(r) exhibited a contact peak and the long-time MSD decreased. These changes in g(r) and MSD, however, occurred at a lower critical concentration of the larger PS (328.9 kDa) in suspensions with binary polymer mixtures than for suspensions with only the 328.9 kDa PS. In samples containing only 328.9 kDa PS, a normalized polymer concentration $C_p/C_p^* \ge 0.96$ was required at $\phi = 0.25$ to obtain a contact peak in g(r) and a decrease in MSD; in samples containing both 6.40 kDa and 328.9 kDa PS, $C_p/C_p^* \ge 0.53$ of 328.9 kDa PS was required at the same particle volume fraction to obtain a contact peak in g(r). The decrease in critical C_p/C_p^* of the larger PS indicated that the smaller polymer in the binary mixture also contributed to the attractive interaction – even though R_g of the 6.40 kDa polymer was only about 0.3% of the PMMA particle radius.


Figure 2.7: (a-c) Radial distribution function g(r) as a function of r/2a and (d-f) MSD/ $(2a)^2$ as a function of non-dimensionalized delay time $\tau D/a^2$, for PMMA suspensions with various concentrations of 328.9 kDa PS $(C_{p,L}/C_{p,L}^*)$ and fixed concentration of 6400 Da PS $(C_{p,S}/C_{p,S}^*)$.

2.3.2 Comparison of unary and binary mixtures: metrics and normalization

To probe how polymers of different size contribute to the phase behavior of PMMA particles, we compared the structure and dynamics across sets of samples containing small, large, or both PS (Table 2.2). Determining the effects of depletant size and dispersity on the phase behavior of the particles across the different sets of samples required quantitative measures for particle structure and dynamics. As metrics for structure, we calculated the coordination number *N* and the particle density fluctuations $\Delta \rho_{10}$ over boxes of size $(10 \ \mu m)^3$. *N* is a measure of the average number of particles whose centers fall within the first coordination shell and hence are in near-contact. Larger values of *N* indicated that, on average, a particle was in close contact with more surrounding particles; hence increasing the particle volume fraction was expected to increase the coordination number. At

constant particle volume fraction, higher values of *N* are consistent with particle aggregation. To calculate coordination number, we determined the location of the first minimum r_{\min} in g(r) for those samples whose pair correlation functions exhibited both a contact peak and an average-separation peak. Subsequently, g(r) was numerically integrated to the average r_{\min} to obtain $N = \int_{0}^{r_{\min}} 4\pi r^{2} \rho g(r) dr$.

Table 2.2: Depletant dispersity (unary/binary) and M_w of the PS depletants added to each sample set.

Sample Set	Symbols in	Unary/Binary	$PS M_w(s)$
	Figures		
U6k	Δ	Unary	6.40 kDa
U300k		Unary	328.9 kDa
B300k		Binary	$328.9 \text{ kDa} + 125 \text{ mg mL}^{-1} 6.40 \text{ kDa}$

In addition to the local structure, we quantified the long-range structural heterogeneity via the particle density fluctuations $\Delta \rho_{10}$ over boxes of side length 10 μ m.^{101,102} The $\Delta \rho_{10}$ metric was calculated via $\Delta \rho_{10} = \frac{\langle N_p^2 \rangle - \langle N_p \rangle^2}{\langle N_p \rangle}$, where N_p is the number of particles in each box. If particles formed large voids during clustering and gelation, the structural heterogeneity was expected to increase above the hard-sphere value of 0.21.^{8,102} Indeed, depletion gels were previously shown to exhibit a local maximum in heterogeneity as a function of the strength of the attraction.¹⁰²

As a metric for dynamics, we examined the value of the MSD at a constant delay time of 10 s, MSD_{10s} ; most samples that exhibited a plateau in MSD reached it by this lag time. Changes in MSD_{10s} reflected changes in the structure and/or dynamics of the suspension. For example, increasing the volume fraction of the particles in the absence of depletant decreased MSD_{10s} , reflecting a decrease in the size of the cage to which particles were localized (Fig. 2.4). Increasing the polymer concentration at constant particle volume fraction also decreased MSD_{10s} , reflecting the slowing of particle dynamics with increasing viscosity or with formation of clusters and gels (Fig. 2.5, 2.6, and 2.7 d-f). To quantitatively compare changes in structure across all sets of samples, we first examined the behavior of *N* as a function of normalized polymer concentration and particle volume fraction. The concentrations of polymers used in this study varied by over an order of magnitude across the different sample sets, requiring normalization of the polymer concentration for effective comparisons. Whereas the concentration of unary PS could be normalized by the overlap concentration of the polymer, this normalization could not be applied directly to samples that contained binary mixtures of PS. We therefore examined several methods to normalize the polymer concentration and thereby compare across unary and binary polymer mixtures.

First, we compared the values of the structural metric *N* as a function of the polymer correlation length. The depletant concentration in most of our samples was above the overlap concentration, so that the polymer solutions were in the semi-dilute regime. In this concentration regime, the strength of the depletion attraction is inversely proportional to the correlation length ξ , ^{103,104} the distance between polymer chains. Samples of similar ϕ and ξ but different polymer dispersity, however, exhibited distinct structures (Fig. 2.8; the colorbar indicates the values of N). Because the correlation length was not able to uniformly describe the observed trends in structure across all sample sets, we posited that the size of the polymer coils affected the structure of the particles even when they were overlapping. To confirm this idea, we normalized the concentration of polymers in binary mixtures by the average overlap concentration $C_{p,\exp}^* = M_w/(4\pi R_{g,z}^3 N_A/3)$, ¹⁰⁵ where $R_{g,z}$ is the z-average radius of gyration of the polymer mixture, and compared the structural metric at similar locations in the (ϕ , $C_p/C_{p, \exp}^*$) plane. This normalization also failed to describe the trends in structure across the sample sets, confirming that the two sizes of PS in the binary mixtures induced depletion attractions as independent polymers, even in the semi-dilute regime (Fig. 2.9; the colorbar indicates

the values of N). Finally, we examined the coordination number as a function of the larger polymer concentration (Fig. 2.10; the colorbar indicates the values of N). Again, the phase behavior was not captured by this concentration across all samples, indicating that the smaller polymer could not be neglected.



Figure 2.8: Color plot of the coordination number *N* as a function of correlation length *ξ* and particle volume fraction *φ* for PMMA suspensions with unary (open) and binary (closed) mixtures of PS added at concentrations above the overlap concentration. Symbol key: △ U6k, □ U300k,
■ B300k.

Although polymer physics suggests that ξ should describe the mixture of polymers, earlier theoretical^{41,72,73} and experimental^{42,43} studies on the effect of depletant dispersity on the phase behavior of colloids suggested that a single size (whether ξ or an average polymer size) was insufficient to describe depletion in highly disperse systems. Instead, knowledge of the depletant size distribution was required to understand the resulting phase behavior. As a simple way to account for the distribution of polymer sizes in our binary mixture, we represented the total PS concentration as a sum of the concentrations of each species in a mixture, normalized by their individual overlap concentrations: $C_{p,N} = C_{p,L}/C_{p,L}^* + C_{p,S}/C_{p,S}^*$, where $C_{p,L}$ ($C_{p,S}$) is the concentration of the larger (smaller) PS in a mixture, and $C_{p,L}^*$ ($C_{p,S}^*$) is the overlap concentration of the large (small) polymer. In the dilute



Figure 2.9: Color plot of the coordination number *N* as a function of polymer concentration normalized by an average overlap concentration and particle volume fraction *φ* for suspensions of PMMA particles with unary (open) and binary (closed) mixtures of PS. Symbol key: △ U6k, □ U300k, ■ B300k.



Figure 2.10: Color plot of the coordination number *N* as a function of larger polymer concentration and particle volume fraction φ for suspensions of PMMA particles with unary (open) and binary (closed) mixtures of PS. Symbol key: □ U300k, ■ B300k.

regime of the polymer ($C_p/C_p^* < 1$) the individual polymer coils do not overlap, and $C_{p,N}$ approximately represents the volume fraction of polymer coils. In earlier theoretical work, the equilibrium phase behavior was shown to be independent of polymer dispersity in the dilute regime under this normalization.^{41,106} In our experiments, however, the polymer concentration in most of the samples was in the semi-dilute regime ($C_p/C_p^* > 1$), where $C_{p,N}$ does not correspond to the volume fraction because the polymer coils overlap. Instead, $C_{p,N}$ sums the individual contributions of both polymers in the mixture. Nonetheless, we found that samples with similar values of $C_{p,N}$ exhibited very similar values of the coordination number across a broad range of polymer sizes and dispersity.

2.3.3 Structural comparisons

To compare the local structure of unary and binary mixtures, we examined the behavior of N as a function of the normalized polymer concentration $C_{p,N}$ and particle volume fraction ϕ . We found that N for all three sample sets collapsed onto a single phase diagram, independent of depletant size or dispersity (Fig. 2.11a; the colorbar indicates the values of N). This agreement suggested that the local structure of the particles depended on the normalized concentration of polymer and not on its dispersity. Further, N did not change significantly with increasing $C_{p,N}$ until the polymer solution was in the semi-dilute regime for the three sets of samples. Although phase transitions are expected at much lower polymer concentrations for hard spheres, ^{11–13} both theoretical^{107,108} and experimental¹⁰⁹ studies showed that increasing the Debye length can shift the phase boundaries to significantly higher concentrations of depletant. In our system, the Debye length estimated from g(r), 480 nm, was much larger than the radii of gyration of the two polymers, 2.8 nm and 23 nm; it was therefore reasonable that no phase transition was observed in our samples at low polymer concentrations.

To compare structure of particles on larger length scales, we also examined the behavior of $\Delta \rho_{10}$ over boxes of size $(10 \ \mu m)^3$ as a function of $C_{p,N}$ and ϕ . The $\Delta \rho_{10}$ metric also agreed closely for all three sample sets as a function of normalized polymer concentration across nearly all of the (ϕ , $C_{p,N}$) parameter space, indicating that the long-range structure of the samples was also independent of polymer



Figure 2.11: Color representation of (a) N and (b) $\Delta \rho_{10}$ as a function of normalized polymer concentration $C_{p,N}$ and particle volume fraction ϕ for PMMA suspensions containing unary (open) and binary (closed) mixtures of PS. Symbol key: Δ U6k, \Box U300k, \blacksquare B300k. (c) Confocal micrographs for samples with similar ϕ and $C_{p,N}$.

dispersity (Fig. 2.11b; the colorbar indicates the values of $\Delta \rho_{10}$). Consistent with the two metrics, micrographs of samples in sample sets U6k, U300k, and B300k revealed similar structures, irrespective of PS size and dispersity (Fig. 2.11c; the micrographs were acquired at a height of $z = 30 \ \mu$ m above the bottom of the sample chamber for sample sets U6k, U300k, and B300k. The three rows of images represent samples with similar particle volume fraction ϕ and normalized polymer concentration $C_{p,N}$.). The greatest disparity in large-scale structure revealed in the micrographs (between sample sets U300k and B300k at a volume fraction of $\phi = 0.25$ and $C_{p,N} \approx 2.5$, Fig. 2.11c, sample a1) was consistent with the region of greatest disparity in the density fluctuations (Fig. 2.11b). To uncover the origin of these disparities, we examined the dependence of the density fluctuations for samples at fixed volume fractions as a function of $C_{p,N}$. Surprisingly, we did not observe a local maximum in $\Delta \rho_{10}$ across the gelation transition seen in the micrographs, which was observed in an earlier study on a similar system;¹⁰² the width of the maximum in that study, however, was smaller than the step size in $C_{p,N}$ used here. At $\phi = 0.25$ and $C_{p,N}$ between 2.5 - 3, the binary sample exhibited an increase in $\Delta \rho_{10}$, which suggests formation of larger voids, and may signal a nearby structural transition (Fig. 2.12b); the corresponding unary samples, however, exhibited little change in $\Delta \rho_{10}$ with $C_{p,N}$. These results suggested that the effects of polymer dispersity on structure may be most pronounced near transition boundaries.



Figure 2.12: Density fluctuations over $(10 \ \mu m)^3$ boxes $\Delta \rho_{10}$ as a function of normalized polymer concentration $C_{p,N}$ for U6k, U300k and B300k. Particle volume fractions ϕ are (a) 0.05, (b) 0.25, and (c) 0.45. The approximate sample-to-sample variability is represented as error bars.

To test the hypothesis that this discrepancy in structure arose due to an incipient transition, we closely investigated cluster formation for the three sample sets at $\phi = 0.25$. Many factors affect clustering and gelation for particles with shortranged attractive and long-ranged repulsive interactions, including the balance between the strengths of the repulsive and attractive interactions, the range of the repulsive interactions, and the particle volume fraction.^{110–115} As metrics to identify the onset of cluster formation, growth, and gelation, we calculated the fraction of particles in the measurement volume remaining as monomers and in the largest cluster; particles were defined to be in a cluster if their nearest neighbor was closer than $r_{\rm min}$. Although all clustered samples must have a largest cluster, we found that samples formed an interconnected gel if a majority (\gtrsim 50%) of the particles in the measurement volume were in the largest cluster. The combination of particle polydispersity and resolution of the tracking algorithm led to a large value of $r_{\rm min}$, so that some monomeric particles were counted as clustered. Thus, the fraction of monomer was less than one for samples without added PS (Fig. 2.13a); in these samples, a vanishing fraction of particles were in the largest cluster, indicating that any apparent clusters remained small (Fig. 2.13b). The dashed lines in Fig. 2.13 are guides to the eye; the error bars represent measured sample-to-sample variability.

This analysis of clustering suggested that samples containing the small PS (U6k and B300k) may gel through a different pathway than samples without small PS (U300k). For the unary large-polymer sample series (U300k), the fraction of monomer decreased starting at $C_{p,N} \sim 0.5$, indicating the formation of small clusters. At this concentration, however, fewer than 10% of particles were in the largest cluster; only when the polymer concentration was increased above $C_{p,N} \sim 1.5$ did the size of the largest cluster grow rapidly. This behavior suggested that formation of small disconnected clusters (at lower strengths of attraction) preceded gelation in this series of samples. By contrast, in samples containing the smaller PS (U6k and B300k), the concentration of polymer at the onset of cluster formation (signaled by the decrease in monomer fraction) nearly coincided with the onset of the increase in size of the largest cluster, near $C_{p,N} \sim 1.2$. This behavior suggested that particles in these samples formed a space-spanning network directly from monomers; here the presence of small polymer appeared to suppress the formation of many small clusters. The transition from monomers/clusters to gels



Figure 2.13: (a) Fraction of monomeric particles and (b) fraction of particles in largest cluster in a sample volume as a function of normalized polymer concentration $C_{p,N}$ for U6k, U300k, and B300k samples at particle volume fraction $\phi = 0.25$.

occurred over normalized concentrations of $C_{p,N} \sim 2 - 3$, where the size of the largest cluster increased rapidly with PS concentration. This transition region corresponded with the region of discrepancy in structure reported in Fig. 2.11b, 2.11c, and 2.12. Nonetheless, the final structure of the gels in all sample sets (at high polymer concentrations) was similar despite the different pathways to the gel.

To estimate the location of the gelation boundary, we also calculated the cluster size distribution at $\phi = 0.25$. Earlier studies showed that the size distribution of clusters approaches a power law at the gelation boundary.^{15,116} From the behavior of the cluster fraction n(s) as a function of cluster size s for different samples, we estimated that gelation occurred near $C_{p,N} \approx 1.4 \pm 0.2$ (Fig. 2.14). All B300k

samples studied here exhibited this power-law scaling, precluding the use of this method to determine the gelation boundary. Nonetheless, all samples in the three sets formed gels when $C_{p,N} \ge 1.4$, suggesting that these samples may have similar gelation boundaries. For short-ranged attractions, the phase behavior is expected to be independent of the shape of the interaction potential and to depend only on the reduced second virial coefficient B_2 , per the Law of Corresponding States.¹¹⁷ Indeed, a careful comparison between experiment and simulation in a similar system confirmed that n(s) as a function of s depended only on B_2 .¹⁵ Here, our measurements are consistent with the expectation that the gelation boundaries should coincide for all three sets of samples.



Figure 2.14: Fraction of clusters n(s) of size s as a function of s for the three sets of samples at $\phi = 0.25$.

2.3.4 Dynamics

The dynamics of the particles in sample sets U300k and B300k, as quantified by MSD_{10s} , also largely collapsed onto a single diagram as a function of $C_{p,N}$ and ϕ , irrespective of polymer dispersity (Fig. 2.15; the colorbar indicates the value of MSD_{10s}). The MSD_{10s} of the sample set containing only the smallest PS (U6k), however, did not collapse on the same diagram as U300k and B300k, with the disparity between sample sets most pronounced between samples with $\phi \ge 0.25$ and $C_{p,N} \approx 1$.

To investigate the origin of the disparity in dynamics, we examined the de-



Figure 2.15: Color representation of the mean-squared displacement at 10 s, MSD_{10s} , as a function of normalized polymer concentration $C_{p,N}$ and particle volume fraction ϕ for PMMA suspensions containing unary (open) and binary (closed) mixtures of PS. Symbol key: \triangle U6k, \Box U300k, \blacksquare B300k.

pendence of MSD_{10s} on $C_{p,N}$ for $\phi = 0.05$, 0.25, and 0.45 (Fig. 2.16; the error bars represent sample-to-sample variability). For the samples containing large polymer (U300k and B300k), MSD_{10s} decreased approximately monotonically with $C_{p,N}$. In sharp contrast, the MSD_{10s} did not depend monotonically on normalized polymer concentration for the U6k samples at volume fractions $\phi \ge 0.25$; instead, MSD_{10s} increased concomitant with PS concentration up to $C_{p,N} = 1$, then decreased as $C_{p,N}$ was further increased. Non-monotonic behavior of the MSD with increasing polymer concentration was also observed in the MSD of U6k samples, shown as a function of $\tau D/a^2$ in Fig. 2.6d-f. This behavior was reminiscent of re-entrant melting, observed for hard-sphere particles at higher volume fractions near or above that required for the glass transition.^{118–120} We attributed this behavior to the high effective volume fraction in these samples, which resulted from the strongly repulsive interactions between the particles. To estimate the effects of the repulsions on the effective volume fraction, we estimated the Debye length (κ^{-1}) to be approximately 480 nm. Using an effective particle radius that accounted for the electrostatic repulsions, the effective volume fractions for $\phi = 0.25$ and 0.45 were estimated to be 0.39 and 0.71, respectively. Given the high effective volume fractions, it was reasonable that weak to moderate short-ranged attractions could reduce the time scale required for particles to escape their cages.



Figure 2.16: Mean-squared displacement at 10 s, MSD_{10s} , as a function of normalized polymer concentration $C_{p,N}$ for PMMA suspensions containing unary and binary mixtures of PS at particle volume fractions of (a) 0.05, (b) 0.25, and (c) 0.45.

This re-entrant melting behavior, due to the smaller PS, may also contribute to the shift in $C_{p,N}$ in the onset of cluster formation for U6k and B300k. The increased mobility imparted by the presence of the small polymers may allow particles to remain monomeric up to higher $C_{p,N}$, thus shifting the formation of clusters to higher polymer concentrations. In our charged-sphere system, the melting behavior was only observed for the shorter polymer; in hard-sphere systems, however, re-entrant melting behavior was observed for larger polymer-colloid size ratios than that of our large polymer.^{47,118,119} This comparison suggests that the (modest) disparities between unary and binary mixtures may become less pronounced, or even vanish entirely, if the size of the smallest polymer species exceeds the apparent cutoff for re-entrant effects.

2.3.5 Role of polymer partitioning

Our measurements suggest that quantifying the polymer concentration as $C_{p,N}$, the sum of the individual contributions of each polymer in a binary mixture, led to close agreement of structure and dynamics between samples with unary and binary mixtures of depletants. This result indicates that both polymers in a binary mixture contribute to the depletion interaction. Earlier theoretical work on the equilibrium phase behavior of depletant systems with a binary mixture of depletants⁴¹ and with polydisperse depletants⁷³ showed that the depletants partition by size into colloid-rich and polymer-rich phases. In these studies, the larger polymers were excluded from the colloid-rich phase.⁷³ This behavior was similar to another entropically-driven phenomenon: partitioning of bimodal polymers within porous media.¹²¹ Theoretical analysis of this partitioning showed that the concentration if the concentration of the larger polymer in the bulk was above its overlap concentration.¹²¹ In that system, the extent of partitioning depended on the normalized concentrations of both species.

Polymer partitioning also has practical consequences for particle aggregation. As one example, the flocculation boundaries of silica particles in the presence of binary mixtures of polymers depended on the order in which the polymers were added to the suspension.⁴² When both polymers were added simultaneously, the flocculation boundary coincided with that obtained when the smaller polymers were added first. This result suggested a physical picture in which the smaller polymer was excluded by its size.⁴² In that study, partitioning was proposed to increase the bulk concentration of the larger polymers, thereby increasing the strength of attraction between the silica particles. Later theoretical work⁴¹ revealed that this partitioning of polymers by size occurred in equilibrium, with more distinct parti-

tioning as the size ratio between the polymers increased.

Based on these earlier studies, we conjecture that our binary system (featuring an order of magnitude difference in the radius of the polymers) partitions into colloid-rich and polymer-rich phases. At the onset of cluster formation, we expect that the smaller polymer would be more concentrated in and around clusters than the larger polymers; the larger polymers would then increase the attraction strength between the clusters as their bulk concentration increased. Hence partitioning of polymers by size could explain the slight discrepancy in the structure and dynamics observed near the fluid-to-solid transition at $\phi = 0.25$. As gels formed, the exclusion of the larger polymer from the colloid-rich phase would increase its concentration in the bulk. The resulting increase in the osmotic pressure could push the gel network closer together to form more compact gels with larger void spaces and would explain the larger density fluctuations of the gels with binary mixtures than with unary depletants (c.f. Fig. 2.12). Furthermore, the trends in cluster fraction in Fig. 2.13 suggest that gels in the binary mixture appeared to form directly from monomers; this pathway may arise from the increased attraction between any temporary clusters that form, due to the increase in bulk concentration of the larger polymer. Effects from polymer partitioning are expected to be most pronounced near flocculation boundaries at which large clusters appeared – and hence did not strongly affect the phase behavior at $\phi = 0.05$ (which never formed gels) or at $\phi = 0.45$ (which did not exhibit large void spaces). Indeed, the overall phase behavior was very similar in the three sample sets when the individual contributions of the polymers in the binary mixture were accounted for using $C_{p,N}$.

2.4 Conclusions

We explored the effects of polymer dispersity on the non-equilibrium phase behavior of colloid-polymer depletion mixtures. The structure (quantified via co-

ordination number N and density fluctuations $\Delta \rho_{10}$) and dynamics (quantified via MSD_{10s}) for samples with short-ranged attractions at similar values of the particle volume fraction ϕ containing unary or binary polymer mixtures could be collapsed onto a single phase diagram as a function of a normalized polymer concentration $C_{p,N}$. The failure to obtain a single diagram using the polymer correlation length or the large-polymer concentration indicated that binary mixtures of PS could not be treated as homogeneous solutions; instead, both sizes of polymer contributed to the effective interaction. Deviations from this picture occurred in two cases: (i) close to the transition from a fluid of clusters to a gel, for which the pathway of gelation varied between sample sets; and (ii) in suspensions of moderate to high particle volume fractions containing only small polymers, which exhibited nonmonotonic changes in dynamics reminiscent of re-entrant melting. These slight discrepancies were consistent with a physical picture in which the polymer partitioned into colloid-rich and polymer-rich phases, suggested by earlier theoretical work on binary polymer mixtures. Hence, if the smaller polymer were closer in size to the larger polymer in the binary mixture, the polymers would partition less and discrepancies would be less pronounced.

The inability of the correlation length to describe the phase behavior of particles in a binary mixture of polymers suggests that the full molecular weight distribution of the polymer must be known to calculate $C_{p,N}$, and thus predict the strength and range of the attraction. Because the phase behavior was independent of polymer dispersity, however, the phase behavior of samples featuring short ranged attractions ($R_g/a < 0.05$) can be predicted once $C_{p,N}$ has been calculated. The independence of phase behavior on polymer size and dispersity may break down for longer-ranged attractions, where the shape of the potential plays a role in the phase behavior, and is an open question for future work. Hence this work suggests that polymers of high dispersity, which are more affordable than uniformly distributed polymers, can be used for applications requiring certain final structures if all polymers in the distribution are small compared to the particles and if the desired phase behavior is far from non-equilibrium boundaries. It also suggests the ability to tune the final polymer concentration by mixing polymers of different sizes to control particle phase behavior.

Chapter 3: Aqueous colloid + polymer depletion system for confocal microscopy and rheology

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For dissertation consistency, the numbers of references, figures, and tables were changed. The captions were shortened for the dissertation.

3.1 Introduction

Colloidal suspensions are useful model systems in which to explore equilibrium and non-equilibrium phase behavior. Micron-sized colloidal particles can be directly visualized in 2-D with light microscopy and in 3-D with confocal microscopy,¹²² and tracked over long times.^{86,123,124} Suspensions of particles with nearly hard-sphere interactions exhibit equilibrium fluid and crystal phases, in agreement with the behavior expected for hard spheres, and form a non-equilibrium glass when rapidly concentrated.¹²⁵ Microscopic imaging experiments on hard-sphere colloidal suspensions have therefore been used to explore processes involved in transitions to or from crystals,^{126–131} and to test theoretical predictions for the glass transition.^{132–137} Inducing an attraction between particles, for example by adding a non-adsorbing depletant,⁹ shifts the equilibrium phase boundaries.¹² Depletion interactions can also generate other kinds of nonequilibrium solids such as attractive glasses⁴⁸ and colloidal gels,^{83,102} whose mechanical properties depend upon the strength and nature of the interparticle attractions. Imaging experiments, in this context, allow the microscopic particle structure to be linked to the macroscopic mechanical properties. 138,139

While many fundamental studies of colloidal phase behavior are carried out in quiescent conditions, practical and technological applications of colloidal suspensions often involve flow. Microscopy is an essential tool for identifying processes at the particle scale that control the bulk flow properties. Confocal imaging studies, for example, reveal that sheared hard-sphere colloidal crystals may change their local structure¹⁴⁰ or melt entirely,¹⁴¹ with the dynamics of crystallization and melting distinct from those under quiescent conditions.¹⁴² Hard-sphere colloidal glasses in shear flow exhibit strongly localized yielding,¹⁴³ leading to shear-banding,^{144,145} or jamming and self-filtration.¹⁴⁶ Finally, colloidal gels deform non-linearly¹⁴⁷ and yield under shear flow.^{139,148} Single-particle imaging also aids in elucidating the contribution of hydrodynamic forces versus short-range repulsions¹⁴⁹ and of normal stress differences to particle migration¹⁵⁰ in sheared or flowing hard-sphere colloids. The design of practical suspensions, however, often requires the interactions between particles to be tailored to control microstructure as well as rheological properties,¹⁵¹ such as viscoelasticity or normal stress differences. Connecting the changes in 3-D microstructure to the resulting macroscopic flow properties is thus facilitated by model systems compatible with 3-D confocal imaging and demanding rheological tests.

The most common model system used for 3-D confocal imaging is a suspension of poly(methyl methacrylate) (PMMA) particles,⁸¹ sterically stabilized with short poly(12-hydroxystearic acid) (PHSA) polymers, in organic solutions of similar density and index of refraction. Index- and-density-matching solutions used for these PMMA particles include a binary mixture of decahydronaphthalene (decalin) and either bromocyclohexane or bromocycloheptane,^{15,83,132,152} or a ternary mixture of *cis*-decalin, tetrahydronaphthalene (tetralin), and carbon tetrachloride.⁴⁹ Polystyrene (PS) is soluble in these mixtures and does not adsorb on the PMMA particles,¹⁵³ leading to adjustable depletion attractions in an index- and densitymatching solvent.⁸³ Many variations of this system have been developed, including crosslinked PMMA particles,¹⁵⁴ PS-core / PMMA-shell particles,¹⁵⁵ and PMMA stabilized by poly(dimethylsiloxane)¹⁵⁶ or copolymer (diphenyl-dimethyl) siloxanes.¹⁵⁷ Although the PMMA system provides convenient tunability, the particles may become highly charged in the organic solvents used to match their refractive index and density.¹⁵² While certain salts are soluble at low concentrations in the organic solvents and hence in principle could be used to screen repulsions,¹⁵⁸ their limited solubility makes it difficult to fully screen the electrostatic charge and thus control the total interparticle interaction. In addition, the low viscosities of most index-matching solvent mixtures (e.g., 2.3 mPa·s at 20 °C for bromocyclohexane/decalin mixtures) make it very challenging to measure shearstress-sensitive parameters and phenomena, such as normal stress differences and shear thickening, at intermediate particle fractions.^{157,159} An alternative approach is to synthesize particles that can be index-matched in aqueous or polar solvents, in which electrostatic repulsions can be screened by adding salt. Silica particles, for example,^{160,161} can be index-matched in aqueous mixtures of glycerol or dimethyl sulfoxide,^{162–164} but unfortunately cannot be density matched to avoid gravitational sedimentation. Very recently, Kodger, Guerra, and Sprakel prepared copolymer particles [trifluoroethyl methacrylate-co-tert-butyl methacrylate (TFEMA-cotBMA)] that could be index- and density-matched in a mixture of polar sulfolane and formamide and imaged with confocal microscopy.¹⁶⁵ These copolymer particles, compatible with polar solvents, represent a promising route towards the development of a tunable aqueous model system for confocal microscopy.

Here, we characterize an aqueous particle system with controlled depletion attractions that is well suited for confocal microscopy and rheological measurements of normal stress differences. Core-shell TFEMA-*co-t*BMA particles of diameter 1.47 μ m (dispersity D= 0.06) and fluorescent core diameter 0.95 μ m (dispersity D= 0.03) were synthesized following the synthetic protocol reported in Ref. 165. The composition of the particles was selected so that the particles could be refractive index- and density-matched in 80 (w/w)% glycerol in water. We probed the effect of charge screening and depletion attractions on the suspension phase behavior by adding NaCl and polyacrylamide (PAM, $M_w = 186$ kDa) at various concentrations to particle suspensions (Fig. 3.1; DMA: N,N-dimethylacrylamide, SPAm: 2-acrylamido-2-methyl-1-propanesulfonic acid, inimer: 2-(2-bromoisobutyryloxy) ethyl acrylate, SPMA salt: 3-sulfopropyl methacrylate potassium salt). The particles behaved approximately as hard spheres when [NaCl] = 20 mM, but became unstable and aggregated when the concentration of NaCl was further increased. At a fixed salt concentration of 20 mM, changes in the particle structure and dynamics with increasing depletant (PAM) concentration observed at two particle volume fractions ($\phi = 0.05$ and 0.3) followed the trends reported in earlier experiments on depletion-driven gelation of nearly hard spheres.^{83,102} To demonstrate the suitability of this system for rheology, we measured the viscosity and first normal stress difference N_1 of two suspensions at $\phi = 0.4$ with and without added polymer. The moderate solvent viscosity (55 mPa·s at 20 °C) facilitated measurements of N_1 and eliminated the onset of instabilities such as secondary flows or edge fracture, and addition of polymer slightly increased N_1 . This system hence represents an alternative to the common PMMA/PS model system for investigating phase behavior and flow properties in attractive colloidal suspensions.

3.2 Materials and methods

3.2.1 Synthesis of particles

To synthesize poly(2,2,2-trifluoroethyl methacrylate-*co-tert*-butyl methacrylate) core-shell particles, we followed the protocol described in Ref. 165. Briefly, this protocol included: (1) synthesis of fluorescent particle cores; (2) growth of non-



Figure 3.1: Illustration of the depletion model system. Copolymer core-shell particles were stabilized in aqueous solvents by short charged polymer chains. Addition of polyacrylamide to the solution induced a depletion attraction between the particles.

fluorescent shells on the particles; (3) growth of charged stabilizer polymers on the surface. Unless stated otherwise, all chemicals were purchased from Sigma Aldrich.

First, fluorescent, cross-linked core particles were synthesized with a volumetric ratio of 2,2,2-trifluoroethyl methacrylate (TFEMA; Synquest Laboratories) to *tert*-butyl methacrylate (*t*BMA) of 45:55, chosen to refractive index- and densitymatch 80 (w/w)% glycerol in water. Fluorescence was incorporated by co-reacting rhodamine-B-methacrylate, which was synthesized from rhodamine B and glycidyl methacrylate according to Ref. 165. Ethylene glycol dimethacrylate was co-reacted with the monomers to cross-link the core. The solvents were methanol and water. Volumes and/or masses of each component used in the reaction are summarized in Table 3.1. An initiator-monomer (inimer), 2-(2-bromoisobutyryloxy) ethyl acrylate, was synthesized according to Ref. 165. This molecule was incorporated into the core and shell of the particles as a monomer, so that it could be used as an initiator for the growth of charged surface polymers in the last stage of particle

synthesis.^{165,166} All components (TFEMA, *t*BMA, ethylene glycol dimethacrylate, inimer, 2,2'-azobis(2-methylpropionitrile), 3-sulfopropyl methacrylate potassium salt, fluorescent monomer, methanol, and water, Table 3.1) were loaded into a 500 mL single-neck round-bottom flask and refluxed with a condenser in an 80 °C oil bath for 5 hours while stirring with a stir bar. Subsequently, the particles were washed and centrifuged 5 times with a 1:1 by volume mixture of methanol and water and stored as a $\phi = 0.2$ suspension in 1:1 methanol:water to be used in the core-shell synthesis.

Non-fluorescent shells, also with a TFEMA:*t*BMA ratio of 45:55, were synthesized onto the core particles with a core:monomer ratio of 1:5 by volume. Poly(vinylpyrrolidone) was added as a steric stabilizer in the shell. Table 3.1 provides the volume and/or mass of each component, all loaded into a 1 L roundbottom flask. The flask was plugged with a rubber septum and nitrogen gas was bubbled through the solution for at least 20 minutes using two needles. The flask was placed in an oil bath, and the bath temperature was raised to 55 °C while nitrogen was bubbled through. The needles were removed after the bath temperature reached 55 °C to prevent the rubber septum from popping off due to pressure build up. The flask was held at this temperature for 16 hours while the contents were stirred with a stir bar. After the reaction, the particles were washed and centrifuged five times in a 1:1 mixture of methanol and water and stored as a $\phi = 0.25$ suspension in the methanol-water mixture.

Finally, controlled-charge co-polymers of 2-acrylamido-2-methyl-1-propanesulfonic acid and dimethylacrylamide were grown on the particle surface using Atom Transfer Radical Polymerization (ATRP).^{165,167} A 1:1 molar ratio of the two monomers was used to generate a negatively charged particle surface. Volumes and/or masses of each component used in this step of the synthesis are summarized in Table 3.2. A sacrificial initiator used to control the size of the poly-

		Core-shell
	Core synthesis	synthesis
2,2,2-trifluoroethyl methacrylate	5.41 g	11.15 g
<i>tert</i> -butyl methacrylate	4.91 g	10.11 g
2,2'-azobis(2-methylpropionitrile)	0.11 g	0.27 g
3-sulfopropyl methacrylate potassium salt	0.11 g	—
Ethylene glycol dimethacrylate	0.22 g	_
Fluorescent monomer (2 wt% in methanol)	2.5 mL = 2.01 g	—
Poly(vinylpyrrolidone) (K30)	_	6.82 g
Cores suspension		
(20 vol% in 1:1 methanol:water)	_	21 mL
2-(2-bromoisobutyryloxy) ethyl acrylate	0.204 mL = 0.29 g	1.26 mL
Methanol	134.6 g	172.75 g
Water	33.9 g	16.7 g

Table 3.1: Mass/volume of each component added to the synthesis of the core particles and core-shell particles.

mer stabilizers, ^{165,168,169} PEGini, was synthesized following Ref. 165. Copper (I) chloride and small volumes of water and methanol were added to a small flask, while the rest of the components were added to a 500 mL flask. Both flasks were sealed with rubber septa with a cannula connecting them. An inlet needle and outlet needle were placed in the smaller and larger flasks, respectively. Nitrogen gas was bubbled through both flasks for at least 20 minutes. Then, nitrogen gas was used to push the Cu(I)Cl suspension into the larger flask, after which the needles and cannula were removed. The larger flask was left to react for 6 hours while stirring with a stir bar at room temperature. After the reaction, the particles were collected and washed by repeated centrifugation with de-ionized water at least 5 times. Then, enough glycerol was added to the particle pellet to result in $\phi = 0.45$ in 60 (w/w)% glycerol in water, assuming that the pellet was at a random-close-packed volume fraction of $\phi = 0.64$. This stock was well-dispersed and then centrifuged, after which the supernatant was replaced with enough glycerol to result in $\phi = 0.48$ in 80 (w/w)% glycerol in water. The well-dispersed particle stock

was centrifuged at 2000*g* for 2 –3 minutes to cream dispersed bubbles, which were carefully scraped off with a clean spatula. The particle stock was then stored at 2 – 5 °C.

	Flask I	Flask II
Copper (I) chloride	0.16 g	-
Copper (II) chloride	-	0.20 g
2-acrylamido-2-methyl-1-propanesulfonic acid		
sodium salt (50 wt% in water)	_	17.3 g
N,N-dimethylacrylamide	_	3.74 g
1,1,4,7,10,10-hexamethyltriethylenetetramine	_	0.73 g
Core-shell suspension		
(25 vol% in 1:1 methanol:water)	-	85.5 mL
Sacrificial initiator (PEGini)	_	1.65 mL = 1.96 g
Methanol	4.20 g	26.1 g
Water	5.08 g	33.1 g

Table 3.2: Mass/volume of each component added to the synthesis of the charged surface polymers.

The resulting particles were nearly refractive index-matched to 80 (w/w)% glycerol in water, such that suspensions could be imaged at least 65 μ m into the sample using a confocal microscope. The particles were density matched to the solvent, such that centrifuging a $\phi \approx 0.05$ suspension for 30 minutes at 5000*g* did not result in any visible changes to the sample.

3.2.2 Zeta potential

We measured the zeta potential of the particles using a Nicomp 380 ZLS zeta sizer (Particle Sizing Systems, Port Richey, FL). The particles were diluted in 9.5 mM Tris buffer (pH \approx 7.5) to $\phi \approx$ 0.001.

3.2.3 Sample preparation for microscopy and rheology

Stock solutions of solvent, polymer, and salt were mixed with the particle stock suspension to make 0.5 mL of final samples for microscopy of varying concentrations of each component. The solvent was 80 (w/w)% glycerol in deionized

water (MilliQ, Millipore). Polyacrylamide (PAM, Polymer Source, $M_w = 185.7$ kDa, $M_w/M_n = 1.40$) and sodium chloride (NaCl, Macron Fine Chemicals) were dissolved in the solvent to make stock polymer and salt solutions, respectively. The final concentrations of PAM in the suspensions were calculated in the free volume.^{10–12} The measured overlap concentration of this polymer in 80 (w/w)% glycerol in water with 20 mM NaCl was 9.93 mg mL⁻¹. We targeted PAM concentrations of 1.75, 5, and 12 mg mL⁻¹, which corresponded to normalized concentrations c/c^* of approximately 0.2, 0.5, and 1.2. After adding each component to a sample vial, the vial was mixed gently using tumbling and/or rolling mixers. Approximately 100 μ L of each sample was sealed in a glass chamber made from coverglass and UV-curable adhesive (Norland Optical). Larger volumes of sample (at least 3 mL) were prepared similarly for rheology. If the mixing procedure entrained bubbles into the sample, the vial was centrifuged at 2000*g* for 2 – 3 minutes to cream bubbles for removal.

3.2.4 Confocal microscopy

A VT Eye confocal scanhead (Visitech, Sunderland, U.K.) connected to a Leica DMI 4000 microscope (Leica Microsystems, Buffalo Grove, IL) equipped with a 100X oil-immersion objective (numerical aperture of 1.4) was used to image all samples. For measurements of the 3-D structure, a series of 2-D images was captured at vertical (*z*) spacings of 0.1 μ m per step at heights of 25 μ m to 65 μ m above the bottom of the sample. At least ten and two such *z*-stacks were collected for each sample at $\phi = 0.05$ and 0.30, respectively. To determine the interaction energy between the particles, 50 *z*-stacks were collected for two concentrations of NaCl (22 mM and 51 mM) at $\phi = 0.01$ with no added polymer. To calculate the radial distribution function *g*(*r*), we used available algorithms in IDL⁸⁶ to locate the centers of particles to submicron accuracy.

To measure the dynamics of the particles, 2-D images were collected as a func-

tion of time at a single *z*-plane. At least two sets of images were collected at 1 frame per second and at 5 frames per second for each sample. For $\phi = 0.05$ samples without depletant, images were collected at 15 frames per second, except at 0 mM NaCl. One sample, with $\phi = 0.05$ and polymer concentration 1.75 mg mL⁻¹, was imaged at 5 and 15 frames per second. We verified that the frame rate did not change the resulting dynamics. To calculate mean-squared displacements, the centers of particles were located and tracked over time using algorithms written in MATLAB.⁸⁷

3.2.5 Rheology

Steady-shear rheology data was collected for two suspensions at $\phi = 0.40$ with 20 mM NaCl in 80 (w/w)% glycerol in water, one with no added polymer and one with 4.96 mg mL⁻¹ in the free volume. All rheology measurements were carried out on a DHR-2 hybrid rheometer (TA Instruments, New Castle, DE) equipped with a hard-anodized aluminum 40-mm diameter, 2° cone and matching 40-mm diameter bottom plate. The temperature was maintained at 20 °C via a Peltier temperature controller. After placing the sample on the bottom plate, the cone was lowered slowly at a rate of 5 μ m s⁻¹ to the trim gap of 62 μ m without exceeding an axial force of $F_N = 0.5 \text{ N}$.¹⁷⁰ If a drop of the sample was ejected from between the plates during this loading protocol, it was observed that the sample eventually became underloaded during preshear, as indicated by a significantly negative axial force ($F_N \leq -0.04$ N). Therefore, just enough sample volume was loaded to allow for minimal trimming, if any. Then, the cone was lowered to the truncation gap of 59 μ m at a rate of 0.5 μ m s⁻¹. We determined, through multiple loadings, that trimming or not trimming the sample did not significantly change the measured rheology beyond sample-to-sample variability. Additionally, if the sample was underloaded, lifting the cone to add more sample volume resulted in erroneous N_1 values but did not affect the viscosity.

A consistent preshear protocol was applied to all samples after loading. The shear was increased from 0.5 s^{-1} to 50 s^{-1} over 30 s, and a constant shear was held at 50 s⁻¹ for 30 s. Then, a weak oscillation (strain amplitude of 0.1% and frequency 1 rad s^{-1}) was applied to the sample for 300 s to monitor the recovery of structure. After the preshear protocol, the axial force was zeroed and the sample was sheared at rates increasing from 0.1 s^{-1} to 800 s^{-1} , with 12 shear rates per decade for the sample without PAM and 6 shear rates per decade for the sample with PAM. At each shear rate up to 100 s^{-1} , the measurement was equilibrated for 30 s and the data were averaged over the next 10 s. Above 100 s^{-1} , the measurement was equilibrated for 5 s and the data were averaged over the next 5 s. The equilibration and averaging times were reduced at high shear rates to avoid significant migration of the particles, which resulted in a transient decrease in the measured viscosity and hysteresis.^{171,172} The shear times were decreased until hysteresis in up and down sweeps in shear rate was effectively eliminated. Hysteresis in N_1 was unavoidable for the colloidal gel sample, most likely due to the changing structure of the gel with shear. At least three fresh loadings of the same sample were measured, and the data at each shear rate during the up sweep were averaged.

The raw first normal stress difference data was corrected for the effects of inertia according to Kulicke *et al.*¹⁷³ It is expected that Newtonian samples, for which $N_1 = 0$, will exhibit negative N_1 values at high shear rates due to inertia. Kulicke *et al.* calculated this inertial N_1 to be proportional to the square of the rotational velocity ω and the square of the radius of the cone R via $N_{1,\text{inertial}} = -3\rho\omega^2 R^2/20$, where ρ is the suspension density. This negative value was subtracted from all measured N_1 values, so that the actual N_1 was higher than the raw N_1 value. Additionally, the N_1 at the lowest shear rate measured $N_{1,0}$ (0.1 s^{-1}) was subtracted from all inertiacorrected N_1 data to correct for baseline values. We confirmed that this inertial correction resulted in a value of $N_1 = 0$ for the Newtonian solvent mixture over

this range of shear rates. Measuring the 80 (w/w)% glycerol in water with 20 mM NaCl with 6 shear rates per decade from 1 s^{-1} to 800 s⁻¹ resulted in a corrected N_1 ranging from -40 Pa to +5 Pa. Then, ±40 Pa can be considered an estimate of the sensitivity of the measurement, which is larger than the vendor-specified instrument sensitivity of 8 Pa (calculated from the 0.005 N axial force sensitivity).

3.3 **Results and discussion**

3.3.1 Zeta and interaction potential

The zeta potential of the particles, measured in Tris buffer, was -76 ± 2 mV. This zeta potential was close to the value of -66 mV measured for similar synthesis and buffer conditions.¹⁶⁵ We measured the interaction potential for dilute suspensions of TFEMA-co-tBMA particles when the electrostatic interactions were screened. For dilute suspensions, the interaction energy potential u(r) is related to the radial distribution function g(r) via $\lim_{\phi \to 0} g(r) = \exp[-u(r)/kT]$.^{174,175} We first calculated g(r) for a suspension with particle volume fraction $\phi = 0.01$ in 80 (w/w)% glycerol in water and a salt concentration of 22 mM NaCl, and then inverted to obtain u(r). For this analysis, 50 independent z-stacks of images, containing $\mathcal{O}(10^4)$ particles, were collected as described in Sec. 3.2.4. The interaction energy, normalized by kT, sharply decreased to near-zero at the average particle diameter and was essentially zero for r > 2a (Fig. 3.2; shaded areas indicate representative error bars). Any attractions or repulsions longer-ranged than r/2a = 1 were minimal (< 0.5kT) and thus insignificant. This result indicates that the TFEMA-co-tBMA particles at low volume fractions behaved approximately as hard-spheres in this solvent mixture. A further increase in the salt concentration to 51 mM NaCl, however, generated a slight attraction between the particles with a potential well depth of $\leq 2 kT$.



Figure 3.2: Normalized interaction energy, u(r)/kT, as a function of normalized radial distance r/(2a). The u(r) was calculated for $\phi \approx 0.01$ suspension in 80 (w/w)% glycerol in water with (a) 22 mM and (b) 51 mM NaCl.

3.3.2 Effect of salt concentration

Next, we examined the effect of the NaCl concentration on the structure of the particles in suspensions formulated at different volume fractions. For salt concentrations below 21.1 mM, confocal micrographs revealed that the particles in a suspension with $\phi = 0.05$ were well-separated (Fig. 3.3; confocal micrographs captured at $z = 30 \,\mu$ m, brightness/contrast adjusted for whole image), consistent with hard-sphere or repulsive interparticle interactions. When the salt concentration was increased to 34.9 mM, the micrographs revealed the formation of small clusters of particles. Nonetheless, the overall similarity of the micrographs in Fig. 3.3 indicated that most particles in suspensions formulated at $\phi = 0.05$ were dispersed such that any cluster formation was localized. The radial distribution function g(r) was consistent with these observations. For salt concentrations of 0 and 21.1 mM, g(r) increased steeply at the particle diameter (i.e. at r/2a = 1), with the slight positive slope of the 0 mM sample indicative of electrostatic repulsion. For salt concentrations of 34.9 and 50.2 mM, g(r) exhibited a modest local maximum at r/2a = 1, indicative of some particle aggregation. The mean-square displacement

(MSD) of all samples, however, increased approximately linearly with the lag time τ and collapsed onto the prediction from the Stokes-Einstein diffusivity D_{SE} of the particles in the glycerol/water solvent (Fig. 3.3c; the dashed line is the calculated MSD for Stokes-Einstein diffusion in 80 (w/w)% glycerol in water with 20 mM NaCl). This result suggests that most particles remained dispersed, even at the highest salt concentration.



Figure 3.3: (a) Confocal micrographs, (b) g(r) as a function of r/(2a), and (c) 1dimensional MSD as a function of delay time for $\phi = 0.05$ suspensions with various concentrations of NaCl. [NaCl] = (a1) 0 mM, (a2) 21.1 mM, (a3) 34.9 mM, and (a4) 50.2 mM.

Upon increasing the particle volume fraction to $\phi = 0.30$, particles were sufficiently close to interact. Confocal micrographs revealed dispersed particles at all salt concentrations, suggesting that any change in structure with increasing salt concentration was insignificant. (Fig. 3.4a, confocal micrographs at $z = 30 \ \mu$ m). The radial distribution function for all samples exhibited a local maximum near $r/2a \approx 1$, reflecting density correlations that emerged due to the formation of a nearest-neighbor shell (Fig. 3.4b). The position of this maximum shifted slightly to lower separations as the salt concentration was increased from 0 to 50 mM but was always slightly greater than the average particle diameter, indicating that electrostatic repulsions were not fully screened at $\phi = 0.30$. The increased particle concentration was expected to affect the particle dynamics. Indeed, the MSD no longer followed the Stokes-Einstein predictions, as particle diffusion was hindered by the

presence of other particles (Fig. 3.4c; dashed line is the MSD calculated for Stokes-Einstein diffusion in 80 (w/w)% glycerol in water with 20 mM NaCl). At a fixed lag time, the MSD decreased as the salt concentration was increased above 20.1 mM. This decrease was slightly larger than expected from the modest increase in solution viscosity with salt concentration, 49.8 mPa·s for 20.0 mM NaCl to 50.9 mPa·s for 50.1 mM NaCl at 24 °C. The decrease in MSD was consistent with destabilization of the particles as electrostatic repulsions were screened and was further supported by the pronounced aggregation observed for particles synthesized with lower surface charge, due to their hydrophobicity. We therefore concluded that the particles behaved as nearly-hard-spheres for NaCl concentrations near 20 mM – without any added salt, the electrostatic repulsions were not screened, whereas at high added salt concentrations the particles were not stable.



Figure 3.4: (a) Confocal micrographs, (b) g(r) as a function of r/(2a), and (c) 1dimensional MSD as a function of delay time for $\phi = 0.30$ suspensions with various concentrations of NaCl. [NaCl] = (a1) 0 mM, (a2) 20.1 mM, (a3) 29.4 mM, and (a4) 50.0 mM.

3.3.3 Effect of polymer concentration

We fixed the NaCl concentration at approximately 21 mM, and next examined the effect of adding polyacrylamide (PAM) depletant on the structure and dynamics of suspensions. In the absence of depletant, particles in a suspension formulated at $\phi = 0.05$ were well-dispersed. Adding PAM at concentrations of 1.76 mg mL⁻¹ and 4.59 mg mL⁻¹ induced the formation of small, compact clusters of par-

ticles (Fig. 3.5; confocal micrographs at $z = 30 \ \mu m$, brightness/contrast adjusted), with the lower concentration of depletant resulting in only localized clusters. Further increasing the polymer concentration to 11.7 mg mL⁻¹ led to a change in the morphology of the clusters from compact to ramified. The radial distribution function confirmed the pronounced changes in particle structure with increasing polymer concentration (Fig. 3.5b): g(r) for polymer concentrations of 1.76 mg mL⁻¹ and 4.59 mg mL⁻¹ exhibited a small and very sharp maximum, respectively, at the particle diameter (i.e., at r/2a = 1), consistent with strong nearest-neighbor correlations. The 4.59 mg mL⁻¹ depletant sample also exhibited a second local maximum at $r/2a \leq 2$. The height of the first maximum for the 4.59 mg mL⁻¹ sample, ranging from 6 – 10, was much greater than that observed in suspensions formulated at $\phi = 0.05$ with varying salt concentration (Fig. 3.3b), further confirming the relatively strong attractions induced by the addition of polymer. The envelope enclosing the maxima in g(r) decayed to 1 for $r/2a \ge 3$, consistent with the fractal scaling of the particle density reported for PMMA/PS depletion gels.⁸³ The g(r)determined for a higher polymer concentration of 11.7 mg mL⁻¹ was similar in shape but the height of the first maximum was lower, consistent with the tenuous clusters (in which particles had fewer nearest neighbors) observed in the confocal micrographs for this sample.

The MSD also exhibited pronounced changes with polymer concentration. In the absence of polymer, the MSD was diffusive and conformed with the Stokes-Einstein prediction for the particles in the glycerol/water solvent (Fig. 3.5c; dashed line is the MSD calculated for Stokes-Einstein diffusion in 80 (w/w)% glycerol in water with 20 mM NaCl). Upon adding polymer, the MSD approached a plateau on short lag times τ , consistent with particle arrest on those time scales; the plateau height decreased as the polymer concentration was increased, consistent with strong bonds between particles. On longer time scales, the MSD increased approx-



Figure 3.5: (a) Confocal micrographs, (b) g(r) as a function of r/(2a), and (c) 1dimensional MSD as a function of normalized delay time $\tau D_{SE}/a^2$ for $\phi = 0.05$ suspensions with 21 ± 2 mM NaCl and various concentrations of PAM in the free volume ((a1) 0, (a2) 1.76, (a3) 4.59, and (a4) 11.7 mg mL⁻¹).

imately linearly as the clusters diffused. The MSDs for the two samples containing polymers at concentrations $\geq 4.59 \text{ mg mL}^{-1}$ collapsed as a function of a normalized time scale $\tau D_{\text{SE}}/a^2$, where D_{SE} is the Stokes-Einstein diffusivity for a particle in the background solution calculated using viscosities of 1.75 mg mL⁻¹, 5 mg mL⁻¹, and 12 mg mL⁻¹ PAM solutions with 20 mM NaCl at 20 °C; this normalization corrects for the background viscosity experienced by the particles. The good collapse indicates that the clusters had similar diffusivities on long time scales.

At a higher particle concentration, $\phi = 0.30$, adding polymer led to the formation of arrested colloidal gels. Confocal micrographs revealed that the particles formed small mobile clusters at low concentrations of polymer, but aggregated to form space-spanning networks when the polymer concentration was increased to 5.36 mg mL⁻¹ (Fig. 3.6a; confocal micrographs at $z = 30 \ \mu$ m, brightness/contrast adjusted; actual volume fraction of the sample with 5.36 mg mL⁻¹ polyacrylamide was $\phi = 0.29$). Consistent with the structural change observed in the micrographs, the location of the first maximum in g(r) shifted to a slightly lower value of r/2aupon addition of a sufficiently high concentration of polymer; additionally, a second local maximum developed at $r/2a \approx 1.8$ (Fig. 3.6b). The MSD of the suspension without polymer was lower than that predicted from the Stokes-Einstein diffusivity of the particles in the background solvent and scaled as a power-law with lag time with an exponent slightly lower than 1, indicating that the high particle concentration slightly hindered the diffusive transport of particles (Fig. 3.6c; dashed line is the MSD calculated for Stokes-Einstein diffusion in 80 (w/w)% glycerol in water with 20 mM NaCl). Upon addition of polymer at concentrations greater than or equal to 5.36 mg mL⁻¹, the particles became dynamically arrested. These measurements confirm that the TFEMA-*co-t*BMA/PAM depletion system exhibits the dynamic arrest observed for colloidal gels in earlier microscopic studies of PMMA/PS depletion mixtures.^{15,102,176}



Figure 3.6: (a) Confocal micrographs, (b) g(r) as a function of r/(2a), and (c) 1dimensional MSD as a function of normalized delay time $\tau D_{SE}/a^2$ for $\phi \approx 0.30$ suspensions with 20.0 ± 0.6 mM NaCl and various concentrations of PAM in the free volume ((a1) 0, (micrograph not shown) 1.51, (a2) 1.75, (a3) 5.36, and (a4) 11.7 mg mL⁻¹).

3.3.4 Rheological measurements

The microscopic measurements reveal that this system undergoes a transition from a fluid to a gel as the concentration of polymer (and hence the strength of the depletion attractions) is increased, qualitatively consistent with the behavior observed in earlier studies. To confirm that this system is also well suited for measurements of normal stress differences, one challenging rheological test, we formulated two suspensions with a slightly higher particle volume fraction $\phi = 0.40$ and NaCl concentration of 20.1 ± 0.1 mM. The sample with $\phi = 0.40$ without polymer was a dense colloidal fluid, and the location $(r/2a \approx 1.1)$ and height $(g(r) \approx 1.7)$ of its first local maximum in g(r) were close to those of the slightly less concentrated ($\phi =$ 0.30) sample shown in Fig. 3.4. The sample with $\phi = 0.40$ and PAM concentration of 4.96 mg mL⁻¹ was an arrested colloidal gel.

Using a cone-and-plate geometry, we measured the viscosity and the corrected first normal stress difference $N_1 - N_{1,0}$ as a function of the shear rate for the suspensions at $\phi = 0.40$ with and without polymer depletant. In the absence of the PAM polymer, the suspension viscosity ranged from 0.3 and 0.4 Pa·s across a shear rate range of $0.1 - 800 \text{ s}^{-1}$, decreasing very slightly as the shear rate was increased from 0.1 to 100 s^{-1} and then increasing slightly as the shear rate was increased from 100 to 800 s^{-1} (Fig. 3.7a; open squares indicate the measured rheological properties of the solvent; error bars indicate standard deviations over at least 3 measurements). By comparison, the viscosity of a suspension of PMMA particles at a volume fraction of $\phi = 0.40$ in a mixture of bromocycloheptane and decahydronaphthalene (CHB/DHN) without added polymer was 10⁻² Pa·s.¹⁷⁷ The first normal stress difference was approximately zero at shear rates of 0.1 to 10 s^{-1} , and then decreased to -143 ± 9 Pa as the shear rate was further increased, well outside of both the instrument sensitivity (-8 Pa) and the measurement sensitivity (-40 Pa, discussed in Sec. 3.2.5) (Fig. 3.7b). By contrast, in the less-viscous CHB/DHN solvent used with PMMA nearly-hard-spheres, the normal stresses are not measurably different from zero across the accessible range for similar ϕ .¹⁷⁷

Upon adding polymer, the viscosity of the suspension became shear-thinning, as previously observed for PMMA/PS depletion gels.^{19,178} The corrected N_1 was nearly zero over the same range of shear rates (0.1 to 10 s^{-1}) as for the suspension with no added polymer, then decreased only to -90 ± 30 Pa as the shear rate was further increased. This result indicates that addition of polymer modifies the development of the first normal stress difference; we will systematically explore this


Figure 3.7: (a) Viscosity and (b) corrected first normal stress difference as a function of shear rate for suspensions with $\phi = 0.40$ in 80 (w/w)% glycerol in water, 20.1 ± 0.1 mM NaCl, and the indicated concentration of polymer.

dependence in a future study. These measurements confirm that our aqueous particle/polymer system is well suited for combined confocal and rheological studies aimed at elucidating the microscopic mechanisms driving nonzero normal stress development.

3.4 Conclusions

By tuning a newly-developed particle system¹⁶⁵ to be index- and densitymatched to glycerol/water mixtures, we developed and characterized a series of aqueous colloid-polymer depletion mixtures. The TFEMA-*co-t*BMA particles behaved as nearly-hard-spheres at volume fractions of $\phi = 0.05$ and 0.3 in solutions of salt (NaCl) concentration of approximately 20 mM. Upon increasing the concentration of a polymer depletant, PAM, the suspensions exhibited the transition from an equilibrium fluid to a non-equilibrium gel. The moderately high background viscosity of the 80 (w/w)% glycerol solution used to index- and density-match the particles provides high shear stresses even at intermediate particle volume fractions, enabling the evolution of normal stress differences to be observed upon addition of polymer. This system enables combined imaging and rheological measurements of normal stress differences, important for understanding phenomena such as rod-climbing, die swell,¹⁷⁹ drop formation,¹⁸⁰ and particle migration¹⁵⁰ that affect processability of particulate suspensions.

Chapter 4: Contact networks enhance shear thickening in attractive colloid-polymer mixtures

4.1 Introduction

Dense suspensions of particles with repulsive interactions usually exhibit shear thickening, an increase in viscosity with shear rate $\dot{\gamma}$.¹⁸¹ In continuous shear thickening (CST), this increase is gradual and reverses upon decrease in $\dot{\gamma}$. The microscopic mechanisms underlying CST are vigorously debated, with recent studies highlighting both lubrication (hydrodynamic)^{170,182,183} and friction (contact)^{184–189} interactions. The sign of the first normal stress difference N_1 is used to distinguish the contributions from these interactions,¹⁸⁹ with negative and positive N_1 corresponding to lubrication^{190,191} and friction,^{184,192} respectively. Introducing additional interactions between the particles is thus expected to affect shear thickening.

Strong short-range interparticle attractions suppress shear thickening.^{18,25} In continuously shear-thickening colloidal suspensions, this suppression was proposed to arise when the attractive thermodynamic contribution to the viscosity overwhelmed that from hydrodynamic lubrication interactions.¹⁸ Recent simulations of colloidal suspensions with both lubrication and contact interactions challenge this perspective, showing that contact is important even for CST: suspensions with weak interparticle attractions shear thickened, although sufficiently strong attractions still obscured thickening.¹⁹³ None of these studies, however, suggest that interparticle attractions (with possible exception of bridging attractions¹⁹⁴) may enhance shear thickening.

Non-adsorbing polymers added to a colloidal suspension induce short-range depletion attractions, whose stresses can overwhelm thickening.¹⁸ The polymer

itself may also alter suspension rheology. In filled polymers, the elasticity of the polymer medium can dramatically affect N_1 ,^{44,45,159} with increases in shear thickening attributed to particle-induced fluid stresses in elastic polymer solutions.^{195–197} These studies, however, largely treat polymer solutions or melts as continuum fluids and do not consider effects arising from variation in polymer molecular weight or polymer-induced attractions between particles.

In this chapter, we show that polymer depletants added to colloidal suspensions can markedly enhance CST through formation of force-bearing contact networks, depending on polymer molecular weight. Suspensions containing large polymers exhibited a pronounced increase in shear thickening with polymer concentration at dilute to semi-dilute concentrations ($c/c^* \le 1.3$) with an accompanying change in the sign of N_1 . The elasticity (as deduced from N_1) of the background polymer solution was nearly independent of polymer size at these concentrations, indicating that differences in suspension rheology did not arise from changes in background elasticity. Analyzing the results with a friction-based model^{188,189,198} and measuring boundary stress fluctuations,¹⁹⁹ we show that the presence of large polymers increased the fraction of particles in contact, leading to pronounced fluctuations in boundary stress and positive N_1 . This effect arises when the the sheared, extended polymer is large enough to be excluded from the lubrication layers between particles. These results suggest that shear thickening can be enhanced or reduced via addition of non-adsorbing polymers of different molecular weight. This ability to tune shear thickening can be used to probe microscopic mechanisms driving shear thickening and to improve the efficiency of colloidal materials processing.¹⁸¹

4.2 Materials and methods

4.2.1 Sample preparation

Copolymer particles of 2,2,2-trifluoroethyl methacrylate and *tert*-butyl methacrylate (D_H = 1500 nm (PDI 0.1), D_H = 1580 nm (PDI 0.06)) were synthesized¹⁶⁵ to be refractive index- and density-matched to 80 (w/w)% glycerol in water; 20 mM NaCl was added to partly screen electrostatic repulsions between particles. Depletion attractions between particles were induced by adding solutions of polyacrylamide in 80 (w/w)% glycerol/water (Chapter 3) to particle suspensions, such that particle volume fraction ϕ = 0.40 was constant throughout all samples. Three polyacrylamides of various weight-average molecular weight M_w and dispersity Dwere used as depletants: M_w = 185.7 kDa, D= 1.4, Polymer Source (hereafter, USP); M_w = 1.15 MDa, D= 1.8, PolySciTech (ULP); and M_w = 1.97 MDa, D= 21, Sigma Aldrich (DP). The range of the attraction was $R_g/a \approx 0.03 - 0.07$, and the minimum in electrostatic + depletion energy ranged between $\mathcal{O}(-1 \text{ kT})$.

4.2.2 Confocal microscopy and rheology

Suspensions were imaged on an inverted Leica microscope equipped with a VT Eye confocal scanhead (Chapter 3). Measurements of viscosity η and N_1 were performed on a DHR-2 Rheometer (TA Instruments, New Castle, DE) with a 40 mm diameter, 2° hard-anodized aluminum cone, following established protocols (Chapter 3). Selected measurements were verified on a DHR-3 rheometer (TA Instruments) with the same cone and an MCR-301 (Anton Paar USA, Ashland, VA) with 25 mm diameter, 1° stainless steel cone. Varying instrument and cone resulted in identical values of η and N_1 within sample-to-sample variability. A 40 mm parallel plate geometry with 1000 grit sandpaper (3M, St. Paul, MN) attached on both top and bottom surfaces was used to check for slip. The resulting η , when

corrected for gap changes from surface roughness and radial dependence of stress in parallel plates, ²⁰ was the same as that measured using the smooth 40 mm diameter, 2° cone. These measurements confirmed that slip was insignificant in these samples, ²⁰⁰ and that changes in shear thickening did not arise from elastic instabilities. ²⁰¹ Normal stress differences from raw axial force were corrected for inertia ¹⁷³ and initial value measured at the lowest shear rate $N_{1,0}$. The particle Reynolds number²⁰² Re_p $\leq 8 \times 10^{-6}$ indicated that inertial effects on particles were negligible; the geometric Reynolds number²⁰³ Re ≤ 0.05 for suspensions indicated that secondary flows were minimal. At maximum, Re = 2 for the solvent at the highest shear rate, indicating that error from secondary flows should be minimal in all samples.²⁰⁴ The Péclet number (Pe = $(6\pi\eta_0\dot{\gamma}a^3)/(k_BT)$; η_0 is background viscosity, $\dot{\gamma}$ is shear rate, *a* is particle radius, k_B is Boltzmann constant, *T* is temperature) $1 \times 10^1 \leq \text{Pe} \leq 3 \times 10^5$ indicated that stresses arising from Brownian motion could be neglected.

4.3 **Results and discussion**

In the absence of polymer, a colloidal suspension at $\phi = 0.40$ exhibited weak CST at a critical shear stress of 30 Pa and $N_1 \leq 0$ at all accessible shear stresses σ (Fig. 4.1a,d), as expected for dense suspensions of nearly hard spheres.^{170,177,189} Addition of USP at constant ϕ increased the low-shear viscosity of the suspensions and generated pronounced shear thinning for $\sigma \leq 5$ Pa. The shear-thinning exponent n ($\eta \sim \sigma^{-n}$) increased from 0.04 to 1.2 with increasing USP concentration, consistent with shear thinning arising from stronger attractions between particles (Fig. 4.2a; gray lines are guides for the eye).^{20,205} As σ was further increased, the viscosity first reached a plateau and then increased slightly, again displaying weak CST. The shear thickening exponent $\beta = 0.1$ ($\eta \sim \sigma^{\beta}$) in the absence of polymer, and remained constant as USP concentration was increased up to $c/c^* = 1.2$ (Fig. 4.2b). Addition of USP did not markedly alter either shear thickening or N_1 , indicating

that CST arose from formation of hydroclusters. For USP solutions, $N_1 \ge 0$ at high σ in the absence of particles, as expected for polymer solutions, but ≤ 0 in the presence of particles. This result suggests that USP was incorporated in the lubrication layers between particles in hydroclusters, which dominate N_1 .



Figure 4.1: (a-c) Viscosity and (d-f) corrected N_1 as a function of shear stress for $\phi = 0.40$ suspensions with various free-volume concentrations of polyacrylamide (a,d) USP, (b,e) ULP, (c,f) DP. Insets: Micrographs of quiescent suspensions with $c/c^* =$ (d) 0.5 USP, (e) 0.7 ULP, and (f) 0.7 DP (5 μ m scale bars).



Figure 4.2: Power-law (a) shear-thinning (*n*) and (b) shear-thickening (β) exponents as a function of normalized polyacrylamide (USP, ULP, DP) concentration in the free volume c/c^* for $\phi = 0.40$ suspensions.

Addition of ULP resulted in weaker shear thinning but stronger shear thickening at high σ (Fig. 4.1b), as indicated by an increase in β from 0.1 to 0.3. The stronger shear thickening was accompanied by a switch in the sign of N_1 , from negative in hard spheres to positive in ULP, with the magnitudes of N_1 a factor of 10 higher than those observed for nearly hard spheres (Fig. 4.1e). These strikingly different trends in η and N_1 were observed at same ϕ and similar normalized polymer concentration c/c^* in USP and ULP samples, despite similar η and N_1 of the background polymer solutions (Fig. 4.3; $c/c^* = 0$ sample is the solvent with 20 mM NaCl, without polymers or particles) and nearly identical quiescent particle microstructures (Fig. 4.1d,e insets).



Figure 4.3: (a-c) Viscosity and (d-f) corrected N_1 as a function of stress for solutions of (a,d) USP, (b,e) ULP, and (c,f) DP in 80 (w/w)% glycerol in water with 20 mM NaCl in the absence of particles.

Suspensions containing DP, which had comparable number-average molecular weight M_n (M_w) to USP (ULP), exhibited trends in η and N_1 analogous to those of suspensions with ULP. The shear-thinning exponents n of ULP and DP suspensions scaled identically as a function of c/c^* , and were smaller than n values obtained for suspensions containing USP. Shear thinning in attractive suspensions reflects the breaking of bonds between clusters of particles;^{20,205} the smaller n values observed for ULP and DP are consistent with the weaker attractions induced (in equilibrium) by large polymers at fixed c/c^* . Likewise, β values were larger for suspensions containing ULP or DP than for those containing USP, although $\beta \le 0.3$ indicated that all samples were in the CST regime. Further, ULP samples exhibited

larger β values than DP samples. Together, these results suggest that the relatively high M_w of DP and ULP polymers generated the changes in shear thickening and N_1 .

For CST driven by hydrodynamic interactions, β is expected to remain constant as the strength of the attractions is increased,¹⁸ as observed in USP suspensions. In ULP and DP suspensions, however, β increased as c/c^* was increased. The increase in β and change in sign of N_1 (as compared to the hard sphere suspension) observed as c/c^* was increased in ULP and DP samples are, instead, reminiscent of the signatures of contact networks of particles in dense, shear thickening suspensions of hard spheres.¹⁸⁹ Inspired by a theoretical model¹⁸⁸ positing that discontinuous shear thickening emerges when frictional contacts form upon exceeding a critical stress, Ref. 189 postulated that the change in sign of N_1 from negative to positive signals the formation of an interconnected network of frictional contacts throughout the sample. Negative values of N_1 , by contrast, reflect contacts between particles confined within hydroclusters held together by lubrication forces.

To test the hypothesis that contact networks drive the observed changes in rheology for suspensions containing large polymers, the friction-based model of Ref. 188 as modified in Ref. 189,198 was fit to the shear-thickening portion of all viscosity curves. This model posits that the total relative viscosity η_r arises from the competition between two branches of viscosities, each of which diverges when the particles become jammed. In the lower stress branch, particles maintain lubrication layers such that the viscosity diverges at the close-packed ϕ_0 . In the higher stress branch, particle surfaces make contact such that the viscosity diverges at a lower, friction-dependent volume fraction ϕ_m . The viscosity η_r is thus given by

$$\eta_r(\sigma,\phi) = \left(1 - \frac{\phi}{\phi_c(\sigma)}\right)^{-2},\tag{4.1}$$

where the critical volume fraction $\phi_c(\sigma) = f \phi_m + (1 - f) \phi_0$. The fraction of particles in contact $f(\sigma, \phi) = f_{\max}(\phi)e^{-\sigma^*/\sigma \, 189}$ is a function of σ , critical stress for particles to overcome repulsive forces σ^* , and maximum fraction of particles in contact f_{\max} .

The Wyart-Cates model was fit to the shear-thickening portion of all data sets with fixed values of $\phi = 0.40$ and $\phi_m = 0.54$ and bounded $0 \le f_{\text{max}} \le 1$ (because f_{max} is defined as the fraction of particles in the contact network). The ϕ_m value was first determined by performing a global fit over all data sets simultaneously, fixing $\phi = 0.40$ and sharing a variable ϕ_m . For this fit, the initial values were chosen based on expected values for similar hard sphere suspensions¹⁸⁹ ($\phi_m = 0.59$, $f_{\text{max}} = 1$, $\phi_0 = 0.71$, and $\sigma^* = 100$). The resulting ϕ_m with the best fit to all samples was lower than $\phi_m = 0.592$ found in Ref. 189. Small variations in ϕ_m are expected between particle types because the friction coefficients between particles may be different. For the fits shown in Figures 4.4 - 4.6 (from which the fit parameters reported were obtained), independent fits were performed for all sample sets with initial values of $f_{\text{max}} = 1$, $\phi_0 = 0.71$, and $\sigma^* = 100$. Varying the initial value of ϕ_0 to the physically meaningful value of $\phi_{\rm RCP} = 0.64$ and allowing σ^* to vary over an appropriate range of critical stresses for shear thickening (40 – 200 Pa) did not change the resulting fits. The standard deviation in resulting variables was <0.01% for all except ULP samples. For the ULP samples, there was a <0.5% standard deviation in the resulting ϕ_0 and <8% standard deviation in the resulting σ^* . The resulting deviation in the variables for ULP from varying initial values, however, was already captured by the fitting error reported in the thesis. Finally, globally fitting all data sets simultaneously with $\phi = 0.40$ and $\phi_m = 0.54$ resulted in similar standard deviations in resulting variables, but with larger error bars on most fitted parameters.

The friction-based model (Eq. 4.1) quantitatively fit the shear thickening in all samples (Fig. 4.4 – 4.6) using fixed $\phi_m = 0.54^{170}$ and variable ϕ_0 , σ^* , and f_{max} . The



Figure 4.4: Relative viscosity η/η_0 as a function of stress, fitted to a friction-based model^{188,189} for suspensions without polymer and with given normalized concentrations of USP. All suspensions contained $\phi = 0.40$ in 80 (w/w)% glycerol in water with 20 mM NaCl.



Figure 4.5: Relative viscosity as a function of stress, fitted to a friction-based model^{188,189} for suspensions with given normalized concentrations of ULP. All suspensions contained $\phi = 0.40$ in 80 (w/w)% glycerol in water with 20 mM NaCl.



Figure 4.6: Relative viscosity as a function of stress, fitted to a friction-based model^{188,189} for suspensions with given normalized concentrations of DP. All suspensions contained $\phi = 0.40$ in 80 (w/w)% glycerol in water with 20 mM NaCl.

resulting $\phi_0 \approx 0.7$ and $\sigma^* \approx 100$ Pa were independent of c/c^* across all samples (USP, ULP, or DP) (Fig. 4.7a), and comparable to values ($\phi_0 = 0.71$ and $\sigma^* \approx 170$ Pa) reported for hard-sphere suspensions.¹⁸⁹ The near-constant ϕ_0 , the close-packing fraction at which lubricated particles jam, is expected for particles of similar size and dispersity. The comparable values of σ^* obtained here and for hard-sphere suspensions indicates that polymers do not alter the repulsive forces between particles that prevent contact.

Whereas ϕ_0 and σ^* were similar across USP, ULP, and DP samples, f_{max} was notably larger in the presence of ULP and DP. We found $f_{\text{max}} = 1$ for ULP suspensions and $f_{\text{max}} \approx 0.8$ for DP (Fig. 4.7b), but $f_{\text{max}} \approx 0.4$ of USP samples was close to that of the hard-sphere sample. Both β and N_1 exhibited a pronounced increase when f_{max} approached 1 in samples containing large polymers. This increase is similar to the dramatic evolution of β and N_1 when $f_{\text{max}} = 1$ in dense suspensions



Figure 4.7: Fit parameters extracted from Eq. 4.1 as a function of c/c^* , using fixed $\phi_m = 0.54$ (Ref. 170). Dashed lines are guides to the eye at (a) $\phi_0 = 0.71$, $\sigma^* = 100$ Pa, (b) $f_{\text{max}} = 1$. Gray area in (b) represents $N_1 > 0$.

without polymers,¹⁸⁹ and is consistent with the development of a space-spanning network of contacts.

As a second signature of contact network formation, dense suspensions of hard-sphere colloids exhibit pronounced heterogeneities in the boundary stress, reflecting the separation into high-viscosity and low-viscosity fluid phases during CST.¹⁹⁹ Using boundary stress microscopy (BSM), Ref. 199 showed that local fluctuations in the boundary stress arise from a gap-spanning high-viscosity phase. Thus if the enhanced shear thickening in ULP and DP samples arises from an increase in contact networks, increased boundary stress fluctuations are expected as well.

We measured the local fluctuations in boundary stress for representative USP, ULP, and DP suspensions and quantified the average boundary stress as a function of time (Fig. 4.8). Whereas no significant heterogeneities in boundary stress were observed in any sample at low shear rates ($\dot{\gamma} \leq 100 \text{ s}^{-1}$), samples containing large PAM (ULP, DP) exhibited pronounced spatial heterogeneities in boundary stress in the shear-thickening regime (Fig. 4.8a). For $\dot{\gamma} = 100 \text{ s}^{-1}$, fluctuations in average boundary stress remained below 20 Pa (Fig. 4.8b). When the shear rate was increased ($\dot{\gamma} = 500 \text{ s}^{-1}$), USP exhibited more frequent fluctuations, but the magnitude remained low. Samples containing larger polymer, however, developed higher boundary stress fluctuations, with maxima of 89 Pa and 140 Pa in ULP and

DP, respectively. The maximum fluctuation magnitudes were lower than those measured at higher ϕ in concentrated hard sphere suspensions,¹⁹⁹ for which more particles were in the contact network. The increases in magnitude and frequency of boundary stress heterogeneities in ULP/DP samples (compared to USP) are consistent with the idea that the enhanced shear thickening of these samples results from transient contact networks that span the system. Additionally, the stress ratio N_1/σ approaches a constant (Fig. 4.9), which provides further evidence that force chains form in our suspensions containing large polymers (ULP/DP).^{189,206}



Figure 4.8: (a) Examples of boundary stress with weak and strong heterogeneity events. Shared scale bar is 100 μ m. (b) Average boundary stress as a function of time during shear at 100 s⁻¹ (top row) and 500 s⁻¹ (bottom row) for $\phi = 0.40$ suspensions with $c/c^* = 0.7$ USP (first column), ULP (second column), and DP (third column).

The data in Figs. 4.1–4.9 indicate that large polymers modify shear-thickening behavior in colloidal suspensions by inducing contact networks. The increase in contacts does not originate from stronger equilibrium depletion attractions, as the magnitude of the depletion attraction is greater for polymers with lower M_w at fixed c/c^* because of higher polymer number density and thus higher osmotic



Figure 4.9: Comparison of normal stress to shear stress ratio N_1/σ as a function of σ with literature for concentrated hard-sphere suspensions¹⁸⁹ and roughened particle suspensions.¹⁷⁷ Only samples with positive N_1 at high σ are shown. The data from this thesis are for $\phi = 0.40$ suspensions.

pressure.^{10,12,46}

The viscosity data do not show qualitative signatures of even weak, transient bridging of particles by polymers.^{39,194} All PAM solutions exhibited similar values of N_1 in the absence of particles, independent of PAM size (Fig. 4.3). This comparison suggests that the change in sign from N_1 does not arise from increasing contributions from polymer elasticity^{44,159,207,208} and that strain hardening of polymers due to elongational flow around the particles^{195–197} does not drive shear thickening. Finally, measurements of $\phi = 0.45$ suspensions of poly(methyl methacrylate) particles in a dilute, viscous solution of large polystyrene ($M_w \approx 15$ MDa) also showed enhanced shear thickening and change in sign of N_1 from negative to positive compared to hard spheres. Thus, the elasticity of the polymer solution is not responsible for these rheological signatures in our system.

Instead, we posit that the lubrication layers break down^{177,189} when polymers are excluded by size from the gaps between particles, thereby promoting particle contacts. The quiescent radii of gyration of USP and ULP are \approx 20 nm and 46 nm, respectively. To assess the effects of shear on polymer conformation, we calculate a Weissenberg number Wi = $\tau \dot{\gamma}$, where τ is the estimated polymer relaxation time. For suspensions with $c/c^* \approx 0.7$ at $\dot{\gamma} = 100 \text{ s}^{-1}$, Wi_{USP} ≈ 0.1 and Wi_{ULP} ≈ 1.0 , suggesting that both polymers are partially extended.²⁰⁹ The contour length of ULP is ~4 μ m, much larger than the average separation $d \approx 0.3 \mu$ m between particle surfaces at $\phi = 0.40$ estimated from geometric arguments.²⁰² Thus shear may drive exclusion of large polymers from the lubrication layers. By contrast, USP's contour length, ~ 0.6 μ m, is comparable to *d*. USP is therefore unlikely to be shear-excluded by size from between the particles. Indeed, USP and hard-sphere suspensions exhibit similar shear thickening and N_1 , in accord with the idea that USP is small enough to remain entrained within the lubrication layers.

This picture is consistent with experiments^{210,211} and theory/simulations^{212,213} on active microrheology, which show that very strong attractions can arise from non-equilibrium osmotic forces generated when depletants are excluded from gaps between particles. Size-dependent exclusion of polymers is also consistent with the lower $f_{\text{max}} \approx 0.8$ of DP: if the smaller polymers in DP remain entrained in lubrication layers, fewer particles would be expected to make contact. Finally, our exclusion picture is consistent with the filled-polymer literature, ^{44,159,207,208} which states that N_1 is dominated by polymer elasticity and scales as a power-law with σ .¹⁵⁹ This scaling holds for ULP/DP suspensions when $N_1 > 0$, suggesting that polymers contribute independently to N_1 once excluded from interparticle gaps.

Literature studies on filled polymer melts/solutions differ from our work in that the (1) volume fraction of particles are varied at a constant concentration of polymer; (2) the base polymer is generally significantly more elastic than our polymer solutions, which are at dilute to weakly-semidilute concentrations; and (3) the polymer-mediated interactions that arise between particles are usually neglected or only briefly discussed – indeed, particles are typically assumed to be well dis-



Figure 4.10: N_1 as a function of shear stress for (a) ULP and (b) DP samples in the absence ($\phi = 0$) and presence ($\phi = 0.4$) of particles. Normalized concentrations of polyacrylamide in the free volume are given. Solid lines are power laws of exponent 1.67 (average of two exponents in Ref. 159).

persed in the polymer melts or solutions. One key insight from this literature, however, is that N_1 of filled polymers is dominated by the polymer phase.^{44,159,208} If the large PAM in our samples are excluded from the interstices between particles, we expect that the polymer phase should dominate the measured N_1 once $N_1 > 0$. To test this hypothesis, we plot our positive N_1 values as a function of shear stress σ on logarithmic axes (Fig. 4.10). The power-law scaling of 1.67 reported for filled polymers (Ref. 159) is shown for comparison. For ULP samples, N_1 as a function of σ collapses onto a master power-law curve in the presence and absence of particles. This result suggests that the polymer phase dominates the measured N_1 for uniform, large polymers. For the DP samples, there is a slight decrease in N_1 in the presence of particles (similar to filled polymer melts), which suggests that not all of the polymers in DP are excluded from between the particles. In all cases, the power-law scaling is approximately independent of particle concentration as expected from Ref. 159.

4.4 Conclusions

Our results suggest that large polymers promote particle contact networks that enhance CST and change sign of N_1 from negative to positive. Contact network formation represents an additional mechanism by which polymers can alter shear thickening of suspensions, enabling new routes to probe shear thickening. Microscopically, our results are consistent with exclusion of large polymers from lubrication layers, which allows particles to make contact. Insight into non-equilibrium interactions in flowing dense, particle/polymer mixtures is not attainable with current simulation capabilities, but may be accessible in experiments using labeled polymers. The ability to tailor polymer additives and thereby modulate the shear thickening response offers new opportunities in the design of complex materials for technology.^{214,215}

Chapter 5: Bridging attractions with pH-tunable attraction strengths

5.1 Introduction

In earlier chapters of this work, we focused on the phenomenon of depletion attractions, where non-adsorbing polymer additives induced an entropically-driven attraction between the particles. Contrarily, if the polymers adsorb on the surface of the particles, they can form physical bridges by adsorbing on multiple particles simultaneously. Such bridging attractions have been used extensively in industrial applications such as flocculation for water purification²⁷ or other separation processes.²¹⁶ As such, the mechanism of bridging for flocculation have been well studied.^{28–32}

At low concentrations of polymer, the polymers adsorb on more than one particle surface at a time, resulting in bridging attractions. As the polymer concentration is increased, surfaces of the particles become saturated with the polymer, such that the attractions between particles decreases and the particles become stabilized sterically. Then, as the polymer concentration is increased further, depletion attractions can arise from the excess non-adsorbing polymers.³⁷ While bridging attractions have been extensively studied and reported for flocculation, there is still interest in understanding the fundamental phase behavior of this type of attraction, which has island-shaped binodal and spinodal curves,^{33,35} and in particular, comparing this behavior with depletion mixtures at a fundamental level.³³

In addition to the phase behavior, adsorption of polymers on the surface of particles give rise to a rich array of rheological phenomena. For instance, shear thickening can arise due to shear-induced adorption between large polymer and small nanoparticles,^{38,217} or from reversible adsorption of polymers coils on similarly sized particles.³⁹ Shear thinning, yielding, and a seemingly contradictory decrease in viscosity with increasing particle volume fraction has been reported for a mixture of poly(ethylene oxide) with various volume fractions of silica particles.⁴⁰ With the inherent complexity of the mechanism and phase behavior of bridging attractions, it is not surprising that such large variety of rheological behavior has been observed for different types of particle + polymer mixtures. Recently, there have been interest in systematic studies into the effects of polymer adsorption strength on the phase behavior and the resulting effect on rheology of bridging systems, such as PVA composites filled with silica²¹⁸ and using combbrush polymers in suspensions.²¹⁹ However, there is still a lack of a model system that can allow direct comparison of phase behavior and rheology between bridging and depletion attractions.

In this chapter, we discuss the development of a new model bridging system from the same particle suspensions used in earlier chapters to study depletion attractions. These particle suspensions, in the presence of poly(acrylic acid) (PAA) experience bridging attractions. The mechanism of adsorption of PAA on the surface of these particles is likely through hydrogen bonding between the PAA and either or both of the steric and electrostatic stabilizers on the surface of the particles (Chapter 3). The steric stabilizer, poly(vinyl pyrrolidone) is known to undergo strong pH-dependent hydrogen bonding with PAA.²²⁰ The electrostatic stabilizer is a co-polymer of a charged monomer and neutral dimethylacrylamide. Dimethylacrylamide, even when present in a co-polymer, undergoes hydrogen bonding with PAA in acidic conditions.²²¹ As such, it is expected that the adsorption of PAA on the surface of these particles should be very strong at low pH, and become weaker at higher pH values. First, we test this hypothesis through adsorption studies with dynamic light scattering. Then, we investigate the effects of the

changing adsorption strength on the clustering behavior and rheology of these model suspensions. Through developing a model bridging mixture with systematically tunable adsorption strengths, we expect that the fundamental dependence of rheology and phase behavior on the adsorption strength can be studied in the future. Additionally, because the same suspension system is used as the model depletion mixture, systematic comparisons between bridging and depletion mixtures become possible as well.

5.2 Materials and methods

5.2.1 Materials and sample preparation

The particles for this study were poly(2,2,2-trifluoroethyl methacrylate-*co-tert*butyl methacrylate) core-shell particles, synthesized as described in Chapter 3. The hydrodynamic diameter of the particles were 1640 nm (poly 0.04) as measured in water using dynamic light scattering (DLS). The suspensions were prepared from stock suspension and solutions as described in Chapter 3: a $\phi = 0.483$ stock suspension in 80 (w/w)% glycerol in water was mixed gravimetrically with solvent and stock solutions in 80 (w/w)% glycerol in water of sodium chloride, poly(acrylic acid) ($M_v \approx 450$ kDa, Sigma Aldrich), and 50 mM acetate buffer at given pH. The final concentrations of particles, sodium chloride, and acetate buffer were $\phi = 0.15$, 15 mM, and 10 mM, respectively. The concentration of PAA are given in the total sample volume, not correcting for particle volume fraction. The final pH values for suspensions were not measured, so the reported pH values are for the initial pH of the 50 mM acetate stock.

5.2.2 Dynamic light scattering

For PAA adsorption studies using DLS, $\phi \sim 10^{-5}$ particles were suspended in 0, 0.1, and 0.2 mg mL⁻¹ aqueous solutions of PAA in 10 mM acetate and 15 mM sodium chloride at pH 3.8, 4.7, and 5.6. The pH 5.6 sample shifted slightly lower

in pH with the addition of poly(acrylic acid). The scattering was measured on an ALV-GmbH instrument (Langen, Germany) with a 5000 EPP Multiple tau Digital Correlator. Each sample was measured at 75°, 90°, and 105° scattering angles for a total of at least 12 correlation functions collected for 60 seconds each. The bath temperature was 23 °C. The background viscosity of all samples were measured at room temperature (21.9-24.3 °C) using a size 0C Ubbelohde viscometer, taking an average over 5 measurements.

5.2.3 Confocal microscopy

Confocal micrographs were captured as described in Chapter 3 using VT Eye confocal scanhead (Visitech, Sunderland, U.K.) connected to a Leica DMI 4000 inverted microscope (Leica Microsystems, Bufflalo Grove, IL) with a 100X oil-immersion objective (numerical aperture of 1.4). All scale bars are 10 μ m. The images have been brightness and contrast adjusted for visualization.

5.2.4 Rheology

Rheological measurements were performed on $\phi = 0.15$, 0.7 mg mL⁻¹ PAA suspensions at pH 3.8, 4.7, and 5.6 using a DHR-2 rheometer (TA Instruments, New Castle, DE) and 40 mm diameter, 2 degree hard anodized aluminum cone. With the possibility of PAA chain-scission at high shear rates, no preshear was performed; all measurements were performed after a one-hour wait after initial loading.²²² A consistent protocol was followed for each sample: (1) one-hour wait (2) amplitude sweep at 1 rad/s from 0.05 to 50% strain (3) frequency sweeps at 0.07% strain from 50 rad s⁻¹ to 0.5 rad s⁻¹ and 0.5 rad s⁻¹ to 50 rad s⁻¹ (4) flow sweeps from 0.5 s⁻¹ to 500 s⁻¹ and 500 s⁻¹ to 0.5 s⁻¹.

5.3 **Results and discussion**

5.3.1 Adsorption of PAA on particles

To measure the pH-dependent adsorption of PAA on the surface of the particles, DLS intensity correlation functions were measured at multiple scattering angles and PAA concentrations at each pH. For samples without PAA, a singleexponential cumulants function (Eq. 5.1) was fit to the correlation functions. For samples with PAA, a double-exponential decay function (Eq. 5.2) gave better fits to the correlation functions (Fig. 5.1). The function of the single-exponential cumulants used was,

$$g^{(2)} - 1 = \beta \exp(-2\bar{\Gamma}\tau) \left(1 + \frac{\mu_2}{2}\tau^2 - ...\right)^2 + \epsilon, \qquad (5.1)$$

where β was an experimental factor, $\overline{\Gamma}$ was the average decay rate, τ was the experimental delay time, μ_2 was the second moment of the distribution, and ϵ accounted for the noise in the baseline of the data. The double-exponential decay function was,

$$g^{(2)} - 1 = (A_1 \exp(-\Gamma_1 \tau) + A_2 \exp(-\Gamma_2 \tau))^2 + \epsilon,$$
(5.2)

where A_1 and A_2 were amplitudes and Γ_1 and Γ_2 were characteristic decay rates for the two major species.

The extracted decay rates were translated to the diffusion coefficient, D, using the relationship, $\Gamma = Dq^2$, where q is the scattering vector ($q = \frac{4\pi n}{\lambda} \sin(\theta/2)$; here, n is the refractive index (estimated as that of water), λ is the wavelength of the laser (632.8 nm), and θ is the scattering angle). The hydrodynamic diameter (d_H) was calculated from the Stokes-Einstein equation, $d_H = 2r_H = \frac{k_B T}{3\pi\eta D}$, where k_B is the Boltzmann constant, T is the temperature, and η is the background viscosity.



Figure 5.1: Sample correlation function $g^{(2)}-1$ as a function of delay time τ for a $\phi \sim 10^{-5}$ suspension in 0.2 mg mL⁻¹ PAA solution at pH 3.8 (75° scattering angle). Solid lines: fits of single- and double-exponential decays.

All resulting d_H for each sample was averaged, and the 95% confidence interval was calculated. There was approximately a 4% error in the values of d_H from the uncertainty in the background viscosity because of the fluctuations in the room temperature during the viscometer measurements. The error bars in each d_H were estimated as the larger of the 95% confidence interval or the 4% viscosity error.

In the absence of PAA, the d_H of the particles were constant as a function of pH within the experimental errors. In the presence of PAA, there was a clear dependence of the diameter of the larger species ($d_{H,L}$) on the solution pH. At pH 3.8, the larger species in the sample grew significantly with increasing PAA concentration (Fig. 5.2a). As the solution pH increased, the growth in $d_{H,L}$ became less significantly with pAA concentration in any pH condition (Fig. 5.2b).

The smaller species in the particle and PAA mixtures was expected to be the PAA. With increasing pH in the given range, the PAA becomes more charged, and should become larger. Perhaps because of the large dispersity of the polymer sample, however, we did not observe any changes in this smaller species with pH or polymer concentration within the experimental errors. The larger species was expected to be the particles with or without adsorbed PAA. As PAA adsorbs onto the surface of the particles, the particles are expected to become larger. The extent of this growth depends on the amount of the PAA adsorbed and whether the PAA can bridge between more than one particle surface at a time. With stronger, less reversible, adsorption, the size of the larger species should increase more dramatically. Therefore, the $d_{H,L}$ data suggested that the PAA adsorbed strongly on the surface of the particles at pH 3.8, with decreasing adsorption strength as pH was increased.



Figure 5.2: Hydrodynamic diameters of the larger (a) and smaller (b) species in the mixtures of particles and PAA as a function of PAA concentration at various pH conditions. For comparison, the diameter of the particles measured in milliQ water are shown in (a).

5.3.2 Cluster formation as function of pH and PAA concentration

To measure the effect of changing PAA adsorption strength on the phase behavior of the particles, the particle cluster formation at a constant particle volume fraction $\phi = 0.15$ was measured as a function of PAA concentration at pH 3.8, 4.7, and 5.6. The background solution for this study was 80 (w/w)% glycerol in water to refractive index- and density-match the particles for imaging on the confocal microscope. The concentrations of acetate and sodium chloride were 10 mM and 15 mM, respectively.

In accordance with the strongest adsorption of PAA at pH 3.8, large aggregates formed in the presence of 0.7 mg mL⁻¹ PAA (Fig. 5.3a). As PAA concentration increased to 2.3 mg mL⁻¹, the aggregates broke apart into smaller, more mobile aggregates, consistent with PAA beginning to saturate the surface of each particle and making them more stable (Fig. 5.3d).^{36,37} At pH 4.7, PAA adsorbed less strongly on the surface of the particles than at pH 3.8, such that the particles formed smaller, more mobile aggregates at 0.7 mg mL⁻¹ than at pH 3.8 (Fig. 5.3 b). Then, as the concentration of PAA increased, the clusters did not change in size markedly (Fig. 5.3 e). At pH 5.6, consistent with the weakest adsorption of PAA on the particles, smallest clusters formed at 0.7 mg mL⁻¹, and these clusters broke up into almost monomers/dimers at 2.3 mg mL⁻¹ PAA (Fig. 5.3 c,f). These confocal micrographs confirmed that the cluster formation of these suspensions followed the expected phase behavior of bridging suspensions and had a pH-dependence in accord with the pH-dependent adsorption of PAA on the surface of the particles.

5.3.3 Rheology of bridged suspensions

To systematically investigate the effect of PAA adsorption strength on the rheology of resulting suspensions, the rheology of bridging suspensions were measured as a function of pH. All other components were identical across the three



Figure 5.3: Confocal micrographs at $z = 30 \ \mu m$ for $\phi = 0.15$ suspensions with (a-c) 0.7 (± 0.1) and (d-f) 2.3 (± 0.1) mg mL⁻¹ PAA in 10 mM acetate, 15 mM sodium chloride in 80 (w/w)% glycerol in water with pH (a, d) 3.8, (b, e) 4.7, (c, f) 5.6. The scale bars are 10 μm .

samples: $\phi = 0.15$, $c_{PAA} = 0.7$ mg mL⁻¹, 10 mM acetate, 15 mM sodium chloride, in 80 (w/w)% glycerol in water. Additionally, all measurement protocols were identical across the samples such that shear-history would be consistent as well (Sec. 5.2.4).

At pH 4.7 and 5.6, the samples remained liquid-like, such that oscillatory measurements were only possible in a very narrow range of amplitude and frequency values. At pH 3.8, the oscillatory measurements were not reproducible, with gellike to liquid-like behavior at different loadings. This lack of reproducibility may have arose from the chain-scission arising in these samples, as discussed below. As such, the oscillatory data are not reported here for any of the samples.

Contrarily, the flow curves with steady shear had excellent loading-to-loading reproducibility across all three samples (Fig. 5.4). For two sample loadings each, an average value was calculated in the upward and downward sweeps of shear rate, and the error bars were calculated as half of the range of data at each shear rate. With increasing shear rates, all three samples exhibited weak shear-thinning, consistent with the breakage of clusters that formed at this PAA concentration. The low-shear viscosity values trended with the strength of adsorption, such that pH 3.8 had the strongest adsorption strength of PAA and the highest low-shear viscosity.



Figure 5.4: Viscosity as a function of shear rate for $\phi = 0.15$ suspensions with 0.7 mg mL⁻¹ PAA. The solution pH were (a) 3.8, (b) 4.7, and (c) 5.6. Upward and downward sweeps are filled and hollow symbols, respectively.

Upon decreasing the shear rate, pH 4.7 and 5.6 samples had minimal hysteresis, such that the viscosity increased back to the initial values. At pH 3.8, the viscosity during the downward sweep in shear rate was significantly lower than during the upward sweep, such that it was closer to the viscosity values at pH 5.6. This drastic change in viscosity of pH 3.8 suspension in the upward and downward sweeps of shear rate indicated that the interactions between the particles decreased significantly in this sample after being sheared at high shear rates.

Similar decrease in viscosity was observed in the past for strongly bridging suspensions when the polymer chains were shown to undergo chain-scission with high shear.²²² In such cases, chain-scission led to weaker bridging between the particles. This picture was consistent with the behavior of the pH 3.8 sample. At this pH, PAA adsorbed most strongly on the surface of the particles. Then, when high shear was applied, the adsorption weakened, such that the sample viscosity

resembled that of the sample with weakest bridges (pH 5.6). The chain-scission for pH 3.8 samples also may explain the lack of reproducibility in the oscillatory measurements for this sample, because inconsistent shear is applied during sample loading as well.

5.4 Conclusions

The interaction between particles in a particle + polymer mixture is dependent on the strength of adsorption of polymer on the particle surfaces, with the extremes of depletion (not adsorbing) and irreversible bridging (strong adsorption) attractions. In this chapter, we developed a model colloid + polymer mixture with pH-dependent adsorption of polymer. We showed that the polymer adsorption strength decreased with increasing pH, and this decrease reflected in both the cluster formation and rheology of the suspensions. This model system allows for future systematic studies on the effects of bridging strength on the phase behavior and rheology. By tuning both the ratio of polymer to particle size and the concentrations of polymer and particle, interesting phenomena are expected to arise as a function of polymer adsorption strength.^{38–40,217}

Chapter 6: Conclusions and future work

In this work, we studied the effect of polymer additive size, dispersity, and adsorption strength on the phase behavior and rheology of model colloids with polymer-mediated attractions. Through systematic comparisons across identical suspensions with only one variable at a time, we were able to probe some of the complex behavior of colloid + polymer mixtures and open further questions to elucidate the phase and rheology behavior of such mixtures in the future.

6.1 Conclusions

Polymers with finite dispersity are commonly used in most applications. We first measured the effect of polymer dispersity on the phase behavior of a commonly used model depletion mixture. The phase behavior of suspensions with bidisperse mixtures of polymer as depletants agreed closely with that of suspensions with either one of the two uniform polymers. This agreement arose when the concentration of polymer in the mixture was represented as a sum of the contributions of each species ($C_{p,N} = C_{p,L}/C_{p,L}^* + C_{p,S}/C_{p,S}^*$), emphasizing the importance of accounting for each population of polymer in studying the phase behavior, rather than using any average size. Disagreement between the phase behavior of suspensions with bidisperse and uniform polymer depletant was observed near the gelation boundary, where possible polymer segregation by size affected the pathway to gelation. Additionally, the small polymer induced an initial increase in the dynamics of the particles similar to reentrant behavior observed in glassy systems because of the long-range electrostatic interactions between the particles.

To measure the effect of polymer size and dispersity on the rheology (viscosity η and first normal stress difference N_1) of depletion mixtures, we developed a new

model colloid + polymer system without the characteristic long-range electrostatic interactions and low background viscosity of the canonical depletion mixture. To verify that the new system exhibited expected trends for model depletion systems, we measured the structure and dynamics of the particles as a function of salt and polymer concentrations. We were able to form nearly hard-sphere suspensions and depletion gels.

The effects of polymer size and dispersity on the rheology of depletion mixtures were studied with the new model depletion mixture. Three various size polymers were added to an otherwise identical suspension: uniform small polyacrylamide (USP), uniform large polyacrylamide (ULP), and disperse polyacrylamide (DP). In the dilute to weakly semi-dilute concentration regime, the presence of large polymers (ULP, DP) enhanced shear thickening and changed the sign of N_1 from negative (in nearly hard-sphere suspensions) to positive. The mechanism of this change was attributed to the formation of contact networks, as was evidenced from a friction-based model and measurements of boundary stress heterogeneities. The contact networks likely formed because of the size-dependent exclusion of large polymers from the lubrication layers between the particles at high shear rates. This exclusion, in turn, can lead to complex interactions between the particles, including strong attractions from nonequilibrium osmotic forces.

Finally, the effect of polymer adsorption strength on the bridging cluster formation and rheology of the model particle suspension was measured using a polyelectrolyte at various solution pH. We showed that the adsorption strength of the polyelectrolyte on the surface of the particles decreased with increasing pH, and this decrease resulted in smaller particle clusters at the same polymer concentration and particle volume fraction. The smaller clusters, then, resulted in lower viscosity values at low shear rates. At the lowest pH studied, the flow curves exhibited likely chain-scission, leading to weaker adsorption after shearing at high shear rates. The ability to tune the strength of polymer adsorption on the surface of a model colloid gives breadth of tunable parameters to systematically examine the rich phase behavior and rheology of polymer-colloid mixtures, such as pH, M_w , salt concentration, ϕ , and polymer concentration, in an otherwise identical suspension.

6.2 Future work

Through this work, we showed that changing the properties of the polymer additive brings forth complex phenomena in both phase behavior and rheology of colloids with polymer-mediated attractions. As such, open questions remain to be further studied in the future:

6.2.1 Size-dependent exclusion of polymers

This work highlighted the importance of understanding the size-dependent exclusion of non-adsorbing polymers from between particle surfaces in both quiescent and flowing conditions. This exclusion was thought to drive the change in both the gelation pathway near the phase boundary (Ch. 2) and the extent of shear thickening and sign of N_1 (Ch. 4). However, we were not able to directly probe the exclusion of polymers in our current experimental system.

In quiescent conditions, fluorescently labeled polymers could be used to directly visualize the size-dependent exclusion of polymers during gelation. By using a combination of two different M_w polymers labeled with different dyes, one could image suspensions near the gelation boundary using a confocal microscope to investigate the polymer segregation. Through varying the M_w and concentration ratios, the resulting mechanism of gelation could be distinguished in terms of the amount of polymer segregation by size. The fluorescently labeled polymers could be synthesized by co-polymerizing fluorescently labeled monomers with non-fluorescent monomers.²²³ During flow, investigating size-dependent segregation becomes more challenging. Direct visualization is difficult at the high shear rates required, because of the scan rate limitations of confocal microsopes. Scattering techniques take sampleaverages, such that small changes in concentration throughout the sample may not be detectable. Although indirect, microrheology and microfluidic studies may offer the best option with current techniques.^{210,211} By subjecting a bidisperse solution of polymers to flow with a pair of stationary particles, one could measure the effect of polymer size ratios on interactions between the particles. Concurrently, flowing fluorescently labeled disperse polymers through microfluidic channels with nanoposts arrayed with various gap sizes, one could visualize the segregation of polymers during shear.

6.2.2 Discontinuous shear thickening in the presence of polymer additives

Contact network formation during shear was a phenomenon first observed in granular materials.¹⁸⁴ Due to the frictional interactions between particle surfaces, these networks led to positive N_1 and discontinuous shear thickening ($\eta \sim \sigma^1$). Our suspensions with large polymers exhibited enhanced shear thickening, but the shear thickening remained continous. In studying the effects of contact network formation in the shear thickening of suspensions, increasing ϕ to values where the shear thickening exponent β is near 1 and adding large polymers would give further insight into the thickening phenomenon for attractive suspensions. Additionally, even small amounts of the large polymer led to enhanced shear thickening, so this may be a useful method to induce discontinous shear thickening without increasing the overall viscosity significantly.

6.2.3 Rheology of strong bridging gels

Rheological behavior of bridging systems have been shown to exhibit a rich array of behaviors depending on many factors: size ratio between particle and polymer, concentrations of particle and polymer, and adsorption strength of polymer on the surface of particles. With the newly developed model system, it would be possible to study the rheology of strongly to weakly bridging gels under all the same conditions except pH, and hence the strength of adsorption of polymers. This would then, give further insight into the specific factors that give rise to such rheological phenomena as shear thickening, thixotropy, and negative thixotropy observed in literature for bridging systems.^{38–40,217}

6.2.4 Phase behavior of pH-dependent bridging to depletion suspensions

As with the rheological behavior, the phase behavior of colloid + polymer mixtures can exhibit a rich array of phenomena depending on the adsorption strength of the polymers on the surface of the particles. Although not explored in this work, it is expected that as the polyelectrolyte becomes completely charged at high pH, it should no longer adsorb on the surface of the particles. This is because the mechanism by which the polyelectrolyte adsorbs on the surface of the particles is by hydrogen bonding to the surface polymer brushes, and it should no longer hydrogen bond to these brushes at higher pH values. Under these conditions, depletion attraction should be recovered. As such, using an otherwise identical particle + polymer suspension, we can access phase behavior of strong, irreversible bridging to weak bridging, to depletion attractions by only changing the solvent pH. This would allow direct comparisons between bridging and depletion attractions, which is difficult to do systematically when other factors are changing between the samples simultaneously.

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