# Mechanical Failure in Colloidal Gels

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Mechanical Failure in Colloidal Gels

A dissertation presented
by
Thomas Edward Kodger
to
School of Engineering and Applied Sciences
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in the subject of
Applied Physics

Harvard University
Cambridge, Massachusetts

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Mechanical Failure in Colloidal Gels

Abstract

When colloidal particles in a dispersion are made attractive, they aggregate into fractal clusters which grow to form a space-spanning network, or gel, even at low volume fractions \( \phi \). These gels are crucial to the rheological behavior of many personal care, food products and dispersion-based paints. The mechanical stability of these products relies on the stability of the colloidal gel network which acts as a scaffold to provide these products with desired mechanical properties and to prevent gravitational sedimentation of the dispersed components. Understanding the mechanical stability of such colloidal gels is thus of crucial importance to predict and control the properties of many soft solids. Once a colloidal gel forms, the heterogeneous structure bonded through weak physical interactions, is immediately subject to body forces, such as gravity [1], surface forces, such as adhesion to a container walls [2] and shear forces [3]; the interplay of these forces acting on the gel determines its stability. Even in the absence of external stresses, colloidal gels undergo internal rearrangements within the network that may cause the network structure to evolve gradually, in processes known as aging or coarsening [4, 5] or fail catastrophically, in a mechanical instability known as syneresis.

Studying gel stability in the laboratory requires model colloidal system which may be tuned to eliminate these body or endogenous forces systematically. Using existing chemistry, I developed several systems to study delayed yielding by eliminating gravitational stresses through density matching and cyclic heating to induce attrac-
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tion; and to study syneresis by eliminating adhesion to the container walls, altering the contact forces between colloids, and again, inducing gelation through heating. These results elucidate the varied yet concomitant mechanisms by which colloidal gels may locally or globally yield, but then reform due to the nature of the physical, or non-covalent, interactions which form them.
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To family and friends.
Chapter 1

Introduction

Soft Matter as a subfield of physics concerns the states of a system where thermal energy, $k_B T$, plays a large and often dominant role and quantum mechanical effects are unimportant. This is perfectly evident in a colloid, a dispersion of micron-sized objects in a continuum solution. Colloids are encountered in everyday life in the form of paint, milk, mayonnaise, and smoke. In addition to their practical importance, colloidal dispersions are easily observed on millisecond time-scales and micron length-scales while still experiencing phase transitions from liquid, to crystalline or glassy solids as the number of particles per unit volume, or volume fraction, $\phi$, is increased. By combining relatively large time and length scales compared to atomic solids, colloidal dispersions provide a model system for studying such phases of matter, particularly their dynamics and transitions. Crucially, such investigation may be performed with commercially available instruments in three dimensions, either in ‘real-space’ with a confocal microscope, or in ‘reciprocal space’ with light scattering. Of particular current interest in the Soft Matter community is the use confocal
microscopy to observe dynamics within the bulk of a colloidal dispersion on the individual particle length scale. Poorly understood phenomena such as delayed failure of colloidal gels, plastic deformation in glasses, and kinetic arrest in disordered solids are all thought to involve small number of particles; light scattering experiments naturally average over such discrete events. Experimentally, colloidal particles of $1\mu m$ in diameter with a volume of $\sim 1\mu m^3$ dispersed in water thermally diffuse their own diameter in $\sim 1s$. Therefore, confocal microscopy easily images tens of thousand to hundred of thousands of particles in a single microscopic volume of $\sim 100\mu m^3$ with common microscopy objectives. Investigating the equivalent number of thermal elements in computer simulation is extremely difficult.

The simplest colloidal model system interacts with a hard-sphere potential; non-interacting at separation distances larger than the particle radius and infinitely steep upon contact. Volume fraction, $\phi$, is the only dependent variable as particles interact by only volume exclusion[6]. A common model system is monodispersed polymethyl methacrylate, PMMA, particles sterically stabilized by a polyhydroxystearic acid, PHSA, polymer brush and suspended in low dielectric solutions [7]. First synthesized several decades ago [8], this system has been used to investigate the one-dimensional hard-sphere phase diagram as seen in Fig.1.1 [6]. Recent studies using confocal microscopy, with imaging analysis routines to determine the position of particles [9, 10], have explored this simple particle-particle interaction observing a wide variety of fascinating phenomena: the glass transition [11], shear transformation zones [12], shear melting [13, 14], dynamical heterogeneity [15], spinodal decomposition [16], co-crystallization [17], and crystal nucleation [18, 19].
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Figure 1.1: One-dimensional colloidal phase diagram with volume fraction, $\phi$.

Such model colloidal systems should offer excellent control over the particle size and distribution, interparticle interactions, fluorescence and other optical properties. Many of the experimental techniques used for studying colloid suspensions impose constraints: Optical microscopy and light scattering experiments require matching the refractive index of the particles, $n$, to that of the suspending fluid, to minimize optical aberrations and effects from multiple scattering. During rheology measurements, solvent evaporation limits the observable time scales of relaxation processes. In addition to these practical constraints imposed by the experimental methods, minute changes in the magnitude or sign of the interparticle pair potential affect the microscopic structure and dynamics [20, 21, 22]. In most cases, the density of the colloidal particles ideally matches that of the suspending fluid to minimize gravitational stresses. Even minor density mismatches result in density gradients and sedimentation, strongly affecting the behavior of the system [23].

While this PMMA model experimental system has been largely used within the community to study hard-sphere interactions, it can be experimentally limiting. Additionally, these monodispersed PMMA particles are difficult to reproducibly synthesize. Electrostatic interactions often cause deviations from purely hard-sphere interactions in low dielectric medium such as that used for PMMA; this is particularly challenging
to control as charge disassociation is poorly understood [24]. This thesis will discuss an alternative strategy for synthesizing PMMA dispersed in low dielectric solution. I also discuss a completely new experimental system based on a copolymer methacrylate colloid dispersed in a high dielectric constant medium where charge disassociation is well understood. This system also enables previously unattainable studies by controlling the particle buoyancy through changes to the copolymer monomer ratio and by manipulating the interparticle potential by modifying the magnitude and sign of the surface charge.

Colloids which further deviate from a hard-sphere interaction potential aggregate into fractal clusters which grow to form a space-spanning network, or gel, even at low volume fractions $\phi$. These gels are crucial to the rheological behavior of many personal care, food products and dispersion-based paints. Understanding the mechanical stability of such colloidal gels is thus of crucial importance to predict and control the properties of many soft solids. Once a colloidal gel forms, the heterogeneous structure bonded through weak physical interactions, is immediately subject to body forces, such as gravity[1], surface forces, such as adhesion to a container walls[2] and shear forces [3]; the interplay of these forces acting on the gel determines its stability.

Even in the absence of external stresses, colloidal gels undergo internal rearrangements within the network that may cause the network structure to evolve gradually, in processes known as aging or coarsening [4] or fail catastrophically, in a mechanical instability known as syneresis. Syneresis is thought to occur due to inherent internal stresses within the gel network, which is formed by arrested phase separation from
the suspending fluid. While mechanical failure of colloidal gels subjected to external shear or gravitational, has been studied in detail\[3\], catastrophic failure of gels due to internal stresses that accumulate during its formation, remains largely unexplored. As a result, predicting the stability of colloidal gels remains prohibitively difficult. Experimentally studying such behavior require model systems which not only exhibit similar kinetic processes but also allow the experimentalist to efficiently and easily explore relevant parameters.

The purposed of this thesis is to explore the relevant phase phenomena of gels, crystals, and glasses, by first, establishing the ideal experiment to answer a particular question, then second, designing an experimental colloidal system which allows that experiment and lastly, answering that question. The colloidal chemistry explored within this thesis will hopefully open up new avenues of colloidal research.

This thesis is structured into two major sections. First, this thesis discusses the synthesis of model colloidal systems and explores the colloidal phenomena that may be studied experimentally such as opposite charge interaction; crystal-crystal and crystal-liquid surface tension; delayed yielding in colloidal gels; syneresis of gels; and the glass transition. Secondly, non-colloidal soft condensed matter projects are discussed which utilize the functionality of polydimethylsiloxane, PDMS. The thesis is further divided eight chapters:

- Synthesis of non-aqueous PMMA colloids stabilized by PDMS (Chapter 2)
- Synthesis of copolymer colloids for electrostatic experiments (Chapter 3)
- Experimental application of these copolymer colloids, specifically exploring mixed charge interactions (Chapter 4)
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- Colloidal gelation, focusing on gel yielding (Chapter 5)
- Syneresis of colloidal gels (Chapter 6)
- Chemically induced droplet coalescence (Chapter 7)
- Siloxane chemistry in Soft Matter (Chapter 8)
- Imaging liquid to glass transition in emulsions, microgel, and hard-sphere colloids (Chapter 9)
Chapter 2

Synthesis of PDMS stabilized PMMA

Colloidal particles that interact with a hard-sphere potential are a convenient experimental model system for investigating condensed matter phenomena. A common model system is monodispersed polymethyl methacrylate, PMMA, particles sterically stabilized by a polyhydroxystearic acid, PHSA, polymer brush and suspended in low dielectric solutions [7]. First synthesized several decades ago [8], this system has been used to investigate the one-dimensional hard-sphere phase diagram, with volume fraction, $\phi$, being the only independent variable as particles interact by only volume exclusion [6]. While such experiments were limited to bulk, vial-scale experiments, the true power of colloidal model systems lie in the ability to microscopically distinguish each individual thermal element, each particle, within the material. Direct real-space imaging in three dimensions by confocal microscopy along with analysis routines to determine the position of often several thousands of particles has extended the power
of this model system[9, 10, 11, 13, 14, 16, 17, 19, 25, 26, 27].

However, observing deep into the material requires the suspending fluid have a refractive index which matches that of the colloidal particles to minimize scattering and optical aberrations. Additionally, colloids are subject to gravitational stresses arising from a density mismatch between the particle and the suspending fluid. A binary or tertiary mixture of halogenated and non-halogenated liquids simultaneously matches both the refractive index and density of PMMA colloids[28, 29]. However, these obligatory solvents slowly swell the particles over weeks to months causing slow density and volume fraction changes to the particle suspension[30, 31] and continuous loss of the fluorescent dye which labels the particle. The use of covalently linked fluorophores alleviates this problem but introduces charging of the particle and size polydispersity. Crucially, the stabilizing polymer brush, PHSA, is no longer synthesized industrially and has subsequently been investigated in several extensive reports [8, 32, 33], but a consistent synthesis route of the PHSA stabilizer has yet to be established [32].

In this chapter, we describe the synthesis and full characterization of PMMA colloids stabilized by an alternative to PHSA: a polydimethylsiloxane, PDMS brush, schematically shown in Fig.2.1a. We show the brush molecular weight, distribution, and molecular geometry necessary to yield monodispersed particles. Additionally, we synthesize three hydrophobic fluorophores which covalently link to the particle; preventing any loss of image contrast over time. We calorimetrically investigate the slow continual uptake of solvent by the particle and elucidate an accelerated equilibration method termed heat-shocking [34]. Lastly, an equilibrated dispersion in solvent-
Chapter 2: Synthesis of PDMS stabilized PMMA

Figure 2.1: Complete synthesis and visualization of the hard-sphere PMMA particle system. (a) Schematic representation of particle synthesis: the PDMS-PMMA stabilizer is synthesized, then particles, and lastly the stabilizer is locked to the particle surface. (b) Macroscopic images of a heat-shocked particle suspension before and after; the vial is 1cm in width. (c) A single X-Z confocal slice of a random close packed sediment; the coverslip is seen at the bottom of the image.
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Figure 2.2: (a) Schematic of stabilizer synthesis. (b-f) Scanning electron microscopy images of the resulting particles from (b) STAB1, (c) STAB2, (d) STAB3, (e) STAB4 and (f) STAB5 from left to right using the recipes listed in Table 2.1.

Monodispersed hard-sphere colloids offer a convenient means to model the thermo-dynamic phases exhibited by atomic and molecular systems. However, experimentally realizing such an infinitely steep repulsive potential at the surface of the particle is impossible [6]. A good approximate to this potential is achieved through a combination of a repulsive polymeric layer on the particle surface and minimizing van der Waals attraction by matching the refractive index of the colloid to that of the solution. Nearly all colloids are latices, or composed of polymers, which have refractive indices, $n > 1.45$; PMMA, $n = 1.495$ for $\lambda = 589nm$. Due to the low refractive index of water, aqueous mixtures rarely obtain values of $n > 1.45$. Non-aqueous solutions
easily achieve these values due to the high electron densities found in halogenated or conjugated molecules such as tetrachloroethylene, TCE, or toluene respectively. However, most solutions also dissolve the polymers which comprise the colloidal particle. Non-aqueous mixtures of chemicals which match the refractive index of PMMA but do not dissolve PMMA are few [7]. Conversely, the repulsive steric layer must be fully solvated by the mixture. Collapsed or poorly solvated steric layer do not prevent particles from coming into contact where any residual van der Waals forces dominate, resulting in weak to strong attraction. To summarize, hard-sphere colloids must be composed of a material that is refractive index matched to a solution mixture which solvates the surface steric layer without dissolving the particle.

Polyhydroxystearic acid, PHSA, brush polymers have been used as steric layers for PMMA colloids for several decades. However, starting from the monomeric hydroxystearic acid, the brush is challenging to synthesize; variations in molecular weight cause the brush to act poorly as a steric barrier [32, 36]. Alternatively, PDMS is commercially synthesized with ever increasing control and flexibility. It is this widespread commercialization which makes PDMS such an attractive stabilizer for colloidal synthesis. By starting, not from monomer, but from PDMS polymer, the most problematic step in the colloidal synthesis process is bypassed entirely.

2.1 Particle synthesis

We synthesize the steric PDMS brush polymer from a monomer mixture of PDMSmonomethylacrylate, methyl methacrylate, and glycidyl methacrylate as shown in Fig.2.2a. Variation in the PDMS molecular weight and monomer stoichiometry yield
Chapter 2: Synthesis of PDMS stabilized PMMA

a series of brush stabilizers as show in Table 2.1. We then use each stabilizer to synthesize a test colloidal batch; characterization of these test dispersions are shown in Table 2.1 and in Fig.2.2b. Seemingly every alteration to the stabilizer changes the resultant PMMA dispersion in both size and monodispersity; even exact repeats show variation, stabilizers 1 and 2. This undesired sensitivity highlights the difficulty in reproducibly synthesizing PMMA despite starting from highly monodispersed PDMS monomer, with a polydispersity index, PDI= 0.02, defined as \( \sigma/\langle M_w \rangle \), where \( \sigma \) is the standard deviation of the molecular weight, \( M_w \). Interestingly, stabilizer 5 consistently produces colloids with a PDI= 0.07, rough equivalent to the minimum polydispersity require to prevent hard-sphere crystallization in 3D [37]. By relying on a commercial source of PDMS, we eliminate most, but not all, of the synthetic inconsistency.

Using stabilizer 1, the ideal stabilizer stoichiometry, we independently explore changes to the dispersion polymerization synthesis but not stabilizer synthesis. By simply altering the volume fraction of initial methyl methacrylate monomer, we are able to produce a wide range of particles diameters from \( 0.5 – 2.8 \mu m \), all with low polydispersities as shown in Table 2.2 and Fig.2.3. Interestingly, as the weight fraction of monomer increases, we find that the resultant dispersion becomes polydispersed at around \( \phi \sim 48\% \), or close to the onset value for hard-sphere crystal-liquid coexistence [38].
Figure 2.3: Particle diameter (black circles) and polydispersities (gray crosses) as determined by SEM for recipes 1-7 from Table 2.2.
Table 2.1: Composition of particle stabilizers. STAB1 and STAB2 are repeats. a 10kDa PDMS. All particles batches are synthesized using the respective stabilizer according to recipe 6, see Table 2.2. See experimental section for details.

<table>
<thead>
<tr>
<th>Stab.</th>
<th>PDMS</th>
<th>MMA</th>
<th>GMA</th>
<th>AIBN</th>
<th>Molecular Weight</th>
<th>PDI ( M_w/M_n )</th>
<th>Diameter ( \mu m )</th>
<th>CV (N)</th>
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<td>(728)</td>
<td></td>
</tr>
</tbody>
</table>
2.2 Cyanine-based reactive fluorophores

For these PMMA colloids to be used for confocal microscopy experiments, they must be both refractive index matched to the solution and fluorescently labeled. Typically fluorophores are simply kinetically trapped within the colloid, preventing diffusion out of the solid glassy polymer particle. However, most solution mixtures which refractive index match PMMA partially dissolve the polymer. As a result, the fluorophore very slowly diffuses out of the particle over the course of weeks to months leading to a loss in image contrast between the labeled particle and the unlabeled solution. This has been solved by using reactive fluorophores, which copolymerize with the PMMA polymer during particle formation [33]. We synthesize hydrophobic, methacrylate forms of several common cyanine fluorophores, Cy2MM, Cy3MM, and Cy5MM, which are known to have good photostability, high quantum efficiencies, and a wide range of excitation wavelengths as shown in Fig.2.4 and Fig.2.5 [39]. DiI, a commercially available lipophilic form of Cy3, has been used to label PMMA colloids previously; Cy3MM exhibits a nearly identical fluorescence spectra while dissolved in solution as seen in Fig.2.5a,b. Moreover, when covalently bound within the particle, only a slight red-shift is seen in the spectra; the PMMA particle itself absorbs much of the blue excitation from 400 – 500nm as seen in Fig.2.5c. As a consequence, Cy2MM excitation spectra is dominated by this absorption, resulting in far lower fluorescent emission compared to Cy3MM as seen in Fig.2.5d. Cy5MM shows equal fluorescent efficiency to Cy3MM, while having very little spectral overlap as seen in Fig.2.5e; this combination of fluorophores is excellent for two-color experiments.
Figure 2.4: (a) Synthesis scheme of Cy2MM, a DiO analog. (b) Synthesis scheme of Cy3MM, a DiI analog. (c) Synthesis scheme of Cy5MM, a DiD analog.
Figure 2.5: Normalized fluorescence spectra to the maximum excitation or emission intensity. (a) free DiI-C18 fluorophore in solution, (b) Cy3MM in solution, (c) Cy3MM covalently linked inside the PMMA particles, (d) Cy5MM covalently linked inside PMMA particles and (e) Cy2MM in solution. Excitation and emission peaks are noted in the figure for each sample.
2.3 Particle heat shocking

Colloids are affected by gravity which is typically not a concern for atomic and molecular systems; to reduce this gravitational stress, colloids are suspended in solution which match densities. We centrifuge the particles at $\phi \sim 0.20$ into a tertiary mixture of $18/22/60$ by mass of cis-decalin/tetralin/tetrachloroethylene to both refractive index and density match the particle to the solution. However, this solution slowly swells the particle over many months. To accelerate this process, we briefly increase the temperature of the dispersion, a mild form of heat shocking \cite{34}. However, both the appropriate equilibration temperature and equilibration time, $\tau_{eq}$, are unknown.

Using a solution microcalorimeter, NanoDSC TA Instruments, we follow the isothermal swelling of the colloid at different temperatures; the time to reach steady state, $\tau_{eq} = t(Q = 0)$, varies substantially with the set temperature as seen in Fig.2.6a. After equilibration, we measure the colloid $T_g$ by temperature cycling from -20$^\circ$C to 100$^\circ$C at two different heating rates; the resulting $T_g=34^\circ$C represents a substantial drop from the literature value obtained for dried PMMA particles, 98$^\circ$C, as shown in Fig.2.6b and Fig.2.6c respectively. From this $\Delta T_g$, we are able to estimate the mass fraction of the particle that is TCE, assumed to be the primary plasticizer in the mixture, using the empirical relation \cite{40},

$$T_g = T_{g_1}w_1 + T_{g_2}w_2 + Kw_1w_2$$ \hfill (2.1)

where $T_{g_1}$ and $T_{g_2}$ are glass transition temperatures of non-plasticized PMMA=$371^\circ$K and plasticizer TCE=$143^\circ$K \cite{41}, $w_1$ and $w_2$ are the mass fractions of PMMA and
Chapter 2: Synthesis of PDMS stabilized PMMA

TCE, respectively, and $K = -130 \pm 50^\circ K$ an experimentally determined constant for PMMA [42]. We calculate $w_2 = 0.20 \pm 0.03$, depending on the value $K$ which is not directly determined for this solution mixture; this value of $w_2$ is consistent with other estimates [7]. Surprisingly, equilibrated PMMA colloids are $\approx 15\text{vol}%$ plasticizer. For room temperature experiments, only slightly below $T_g = 34^\circ C$, these dispersions could possibly be thought of as highly viscous droplets not rigid spheres. Additionally, this large volumetric swelling highlights why non-covalently linked fluorophores readily leech out of the viscous particles. More difficult to interpret is the enthalpic response during this swelling process which is highly non-monotomic; a small local minimum in the heat flow is seen during the equilibration as shown in Fig. 2.6a. However, we can define $\tau_{eq}$ as the time when the heat flow is approximately 0. We interpret $\tau_{eq}$ to be the diffusive time to swell the particle being dominated by the high internal particle viscosity, $\eta$. For a polymer glass, $\eta \propto e^{(T-T_g)}$; likewise, we find $\tau_{eq} \propto e^{(T-T_g)}$ as shown in the inset of Fig. 2.6a. Based on these calorimetric results, we can establish a heat-shocking protocol: A washed particle suspension at $\phi \sim 0.20$ is placed in an oven at $50^\circ C$ and equilibrated for $>1$ hour. The equilibrated suspension is slightly turbid at $50^\circ C$, but becomes refractive index and density matched when cooled to room temperature, $22^\circ C$.

The fully equilibrated dispersion is stable for years with no change in refractive index or contrast due to a loss of particle fluorophore content. Imaging the dispersion on a confocal microscope is still nontrivial; to minimize any aberrations in 3D imaging, the refractive indices need to be matched for all the sample chamber materials and the dispersion. The refractive index of the equilibrated dispersion is $n = 1.50,$
Figure 2.6: Differential scanning calorimetry (DSC) for PMMA particles. (a) Heat flux from isothermal DSC of a PMMA particle dispersion equilibrating in the refractive index and density matching solution at (—) 40°C, (—) 45°C, and (—) 50°C. (b) Scanning DSC of PMMA particles in suspension after heat shock, $T_g=34°C$. (c) Scanning DSC of dried PMMA particle, $T_g=98°C$
which is slightly higher than literature PMMA due to the swelling of the particle. Rectangular glass capillaries with thin walls, \( d < 200\mu m \), are often used as a quick and inexpensive means to seal and image the dispersion. However, they are exclusively made using borosilicate glass, \( n = 1.47 \), or quartz, \( n = 1.46 \). Coverslip glass has a high refractive index for silicate glass, \( n = 1.515 \) but is ideal for imaging the PMMA system combined with standard oil immersion objectives and immersion fluid, \( n = 1.515 \). To fabricate a flow chamber using coverslip glass, we use a combination of soft lithography and epoxy as depicted in Fig. 2.7. Briefly, a PDMS stamp of nearly any designed geometry is fabricated using soft lithography[43]; the stamp is pressed into a small volume of mixed epoxy resin; after a predetermined time, the stamp is removed, and replaced by a coverslip allowing the resin to fully cure. When designed correctly, the stamp produces a flow channel with its entrance not occluded by the coverslip. The dispersion may be easily loaded into the flow channel and sealed using additional epoxy. The chamber is nearly completely inert to the dispersion with no
Chapter 2: Synthesis of PDMS stabilized PMMA

visible swelling or leaking over many months.

Once sealed, a dispersion with $\phi \sim 0.58$ may be 3D imaged on the confocal as shown in Fig.2.1c. By diluting this dispersion to a volume fraction of $\phi \sim 0.3$, the dispersion acts as a dense liquid. The dynamics of this liquid are acutely sensitive to the interparticle pair potential. We utilize confocal differential dynamic microscopy to measure the dynamics of this dispersion and accurately assess if indeed the dispersion acts like hard-spheres.

2.4 Chapter summary

In this chapter, we synthesize PMMA particles stabilized by a PDMS-brush polymer. By using PDMS pre-polymer and not monomer, we are able to reproducibly form the stabilizer unlike the traditional PHSA. Additionally, we have synthesized three new fluorophores which covalent link to the particle. PMMA particles are then calorimetrically equilibrated with a refractive index and density matching solution which allows 3D confocal microscopy. The uptake of solvent by the colloid is measured and found to significantly drop the $T_g$ of the particles to 34°C, indicating significant and unexpected swelling.

2.5 Experimental for this chapter

All materials were purchased from Sigma-Aldrich and used as received, unless otherwise noted. PDMS-monomethacrylates were purchased from Gelest (5kDa -
Chapter 2: Synthesis of PDMS stabilized PMMA

Table 2.2: Colloidal particle recipes. The following are kept constant: (hexane:dodecane) at a ratio of 2:1 by volume, 1-octanethiol 0.5wt% to monomer, and methacrylic acid (MAAc) at 2wt% to methyl methacrylate (MMA). Column, $\phi$ PMMA, is the assumed volume fraction of PMMA after polymerization. STAB1 is used for all methods. See experimental section for more details.

<table>
<thead>
<tr>
<th>Stab. (g)</th>
<th>MMA (g)</th>
<th>MAAc (g)</th>
<th>Hex. (g)</th>
<th>Dod. (g)</th>
<th>AIBN (g)</th>
<th>CTA (g)</th>
<th>$\phi$</th>
<th>Diam. (µm)</th>
<th>CV (N)</th>
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<td>0.242</td>
<td>0.15</td>
<td>48</td>
<td>4.05</td>
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</table>

MCR-M17 and 10kDa - MCR-M22) and measured to have a $M_w = 5880$ and 10580 with PDI = $\sigma/\langle M_w \rangle = 1.02$ and 1.05, respectively.

2.5.1 Stabilizer preparation

In a typical stabilizer synthesis, PDMS-monomethacrylate, methyl methacrylate (MMA), glycidyl methacrylate (GMA), 2,2’-Azobis(2-methylpropionitrile) (AIBN) and toluene (7.75ml) were predissolved and loaded into a glass syringe, for ratios see Table 2.1. The solution was bubbled for 10 minutes with Argon, inside the syringe. Small diameter non-degrading tubing, such as FEP, was used to connect the syringe to a 100ml 3-neck flask. The flask was charged with ethyl acetate (4.4ml),
butyl acetate (2.2ml) and a small stir bar. A reflux condensor was attached on the middle neck of the flask. The acetates mixture was then heated to 110°C and the syringe contents added at 8ml/hr. After the syringe contents were added, the reaction proceeded for an additional 2 hrs. The stabilizer was cooled and used as-is during the preparation of the colloid.

2.5.2 Synthesis of reactive fluorophores

Free radical polymerizible analogs of DiO, DiI, and DiD: Cy2MM, Cy3MM and Cy5MM, respectively, were each synthesized in three steps adapted from several published sources \[44, 45\]. The synthesis of Cy2MM is schematically represented in Fig.2.4A. 3; 2-methylbenzoxazole, (1, 10mmoles) and 4-bromomethyl phenyl acetic acid, (2, 10mmoles) were added to 1,2-dichlorobenzene (BzCl₂, 50ml) and heated to 110°C for 12hrs. The product was cooled to room temperature, filtered, and washed with acetonitrile (30ml, 3X) to obtain the yellow salt (2.72g, 78%). 5; ethyl-2-methylbenzoxazolium iodide (4, 5mmoles) and diphenylformamide (6mmoles) were added to acetic anhydride (Ac₂O, 15ml) and heated to 130°C for 1hr. Cy2MM; to the uncleaned reaction of 5, pyridine (15ml) and 3 (6mmoles) were added and stirred for 24hrs at 25°C. The solvent was removed under reduced pressure and the product redissolved in chloroform (50ml), dehydrated with sodium sulfate, filtered, and dried under reduced pressure. This intermediate (1.3mmoles) was the esterified; chloroform (CHCl₃, 40ml), 4-(dimethylamino)pyridine (DMAP, 0.4mmoles), 2-hydroxyethyl methacrylate (HEMA, 4.5mmoles) were added to the flask, followed by N,N-dicyclohexylcarbodiimide (DCC, 2mmoles). This final reaction proceeded at
25°C for 24hrs, then filtered, washed with water (200ml) and the organic phase dried and removed under reduced pressure to yield a bright yellow solid Cy2MM, **0.53g**.

The synthesis of Cy3MM is schematically represented in Fig.2.4B. 9; 2,3,3-trimethylindonlenine (6, 33mmoles) and 6-bromohexanoic acid (33mmoles) were added to nitromethane (20ml) and heated to 80°C for 24hrs. The product was precipitated into diethyl ether (150ml), then filtered, and washed with diethyl ether (50ml, 2X) to yield a light red powder (4.84g, 42%). 8; 1,3,3-trimethyl-2-methyleneindoline (7, 5mmoles) and diphenylformamide (6mmoles) were added to acetic anhydride (15ml) and heated to 130°C for 1hr. Cy3MM; to the uncleaned reaction of 8, pyridine (15ml) and 9 (6mmoles) were added and stirred for 24hrs at 25°C. The solvent was removed under reduced pressure and the product redissolved in chloroform (50ml), dried with sodium sulfate, filtered, and dried under reduced pressure. This intermediate (2.9mmoles) was then esterified; chloroform (40ml), DMAP (1.1mmoles), HEMA (12mmoles) were added, followed by DCC (4.4mmoles). This final reaction proceeded at 25°C for 24hrs, then filtered, washed with water (200ml) and the organic phase dried and removed under reduced pressure to yield a bright red solid Cy3MM, **1.18g**.

The synthesis of Cy5MM is schematically represented in Fig.2.4C. 12; 1,1,3,3-tetramethoxypropane (10, 115mmoles), aniline (11, 230mmoles) and 25ml ethanol were heated to 95°C for 10mins [46]. The reaction was cooled and concentrated HCl (25ml) added drop-wise. After addition of ice, the precipitate was filtered with water followed by diethyl ether and dried in vacuum. 12 (6mmoles) and 7 (6mmoles) were added to acetic anhydride (10ml) and acetic acid (10ml), heated to 120°C for 30min-
utes. This intermediate was cooled and the acetic acid removed under vacuum. Then pyridine (15ml) and 9 (6mmoles) were added and allowed to react for 24hrs at room temperature. The product was precipitated in ether (50ml, 3X) and dried. This intermediate (~4.1mmoles) was then esterified; chloroform (40ml), DMAP (1.1mmoles), HEMA (12mmoles) were added, followed by DCC (4.4mmoles). This final reaction proceeded at 25°C for 24hrs, then filtered, washed with water (200ml) and the organic phase dried and removed under reduced pressure to yield a bright purple solid Cy5MM, 2.12g

2.5.3 Colloid preparation

All reactants were added to a 200ml single neck flask with a small stir bar, see Table 2.2; additional reactants were also added at this stage, such as fluorophores (~10mg): DiI-C18 (Invitrogen) or Cy5MM, Cy3MM, and Cy2MM. The flask was fitted with a reflux condenser and submerged into a preheated oil bath such that the air-liquid interfaces of the reaction and oil bath were at the same height; the reaction proceeded at 80°C for 3 hrs. The dispersion was transferred to a 130°C silicone oil bath and the condenser removed. An volume of dodecane was added equal to the initial volume of hexane; the hexane allowed to boil off for 0.5hr. While at 130°C, 50µL of 2-dimethylamino ethanol was added to the flask to lock the stabilizer to the particle surface. The flask was loosely stoppered and allowed to react for 1hr. The dispersion was cooled and washed into decahydronaphthalene by centrifugation for storage.
2.5.4 Particle and stabilizer characterization

Scanning electron microscopy (SEM, Zeiss Supra 55) was used to determine colloid coefficient of variation, CV, defined as the standard deviation over the mean radius, $\sigma / \langle a \rangle$ was always shown as percent, with $N$ being the number of colloids measured, see Tables. A Leica SP5 confocal microscope was used to image the refractive index matched sediment.

2.5.5 Heat-shocking

A particle suspension was washed three times by centrifugation into the tertiary solution of 18/22/60 by mass of cis-decalin/tetralin/tetrachloroethylene, with the final $\phi \sim 0.20$. Solution calorimetry (TA Instruments NanoDSC) was performed with the reference solution being the tertiary solution. Particle equilibration was performed by heating the calorimeter to temperature ($40^\circ$C, $45^\circ$C, $50^\circ$C), then running isothermally measuring the heat flow. Glass transitions temperatures of the equilibrated and dried PMMA particles were measured cycling at $10^\circ$C and $3.3^\circ$C per minute (TA Instruments Q2000 DSC). For bulk heat-shocking, a washed particle suspension suspension at $\phi \sim 0.20$ was placed in a oven at $50^\circ$C for 1 hour. The suspension was slightly turbid after heat-shocking while at $50^\circ$C, but became well refractive index and density matched when cooled to room temperature.

2.5.6 Solvent-resistive sample chambers

Flow channels were fabricated in three steps: mask design, master fabrication, and chamber formation. We used AutoCAD to draw an chamber with eight flow channels
of the desired dimensions as seen in Fig. 7A. This drawing was printed onto a mask transparency such that the flow channels were transparent using CAD/Art, Bandon, OR. Flow channel masters were fabricated using soft lithography from the printed mask as seen in Fig. 7B [47]. Briefly, a silicon wafer was spin coated with a 50 µm thick layer of SU8-3500, which was covered by the transparency mask and exposed to UV. Sylgard 184 PDMS (Dow Corning) was mixed at a 1:10 mass ratio, poured over the master, degassed, and cured at 65°C for 6 hours. The PDMS replica was demolded and kept dust free. 5-minute epoxy (Devon) was mixed and a small volume (∼ 500 µl) was poured onto a cleaned coverslide. The PDMS replica was gently pressed into the epoxy. The epoxy was allowed to cure until a small indentation made in the epoxy retains its shape, approximately 6 minutes. The PDMS replica was carefully peeled from the epoxy and a cleaned 18mm square coverslip, aligned and pressed onto the epoxy such that the inlets were not occluded Fig. 2.7. The device was allowed to cure fully for several hours before filling with the sample dispersion and the inlets sealed with more epoxy. Confocal imaging was performed through the coverslip.
Figure 2.8: Experimental setup for polymerizing the PDMS comb stabilizer. Left, syringe pump set to the above listed flow rate. Syringe contains all monomers and initiator; contents are bubbled with argon prior to loading through the syringe outlet. Right, 3-neck round bottom flask set to 110°C charged with acetates and coupled to a reflux condenser.
Chapter 3

Synthesis of refractive index matched colloids in polar solvents

Model colloidal systems offer excellent control over the particle size and distribution, interparticle interactions, fluorescence and other optical properties enabling 3D confocal microscopy; atomic and molecular phenomena as varied as crystal nucleation[18], vitrification[48] and the dynamics of fluid interfaces[49] are directly visualized on the colloidal length scale. Many of the experimental techniques used for studying colloid suspensions impose constraints: Optical microscopy and light scattering experiments require matching the refractive index of the particles, \(n\), to that of the suspending fluid, to minimize optical aberrations and effects from multiple scattering. During rheological measurements, solvent evaporation limits the observable time scales of relaxation processes. In most cases, the density of the colloidal particles ideally matches that of the suspending fluid to minimize gravitational stresses. Even minor density mismatches result in density gradients and sedimentation, strongly af-
fecting the behavior of the system [23]. By contrast, in other experimental systems controlled sedimentation may enable the experiment [49, 50, 51, 12].

In addition to these practical constraints imposed by the experimental methods, minute changes in the magnitude or sign of the interparticle pair potential affect the microscopic structure and dynamics [20, 21, 22]. In the simplest case, colloids interact through volume exclusion alone; in this so-called hard-sphere limit, only volume fraction, \( \phi \), determines the phase behavior. Three experimental systems exhibit such a hard-sphere interaction potential: unmodified silica in mixtures of polar fluids [12], poly (methyl methacrylate) (PMMA) colloids sterically-stabilized by poly(hydroxystearic acid) dispersed in a mixture of low dielectric organic solvents [21, 22] and stearylated-silica dispersed in decalin or higher alkanes [52]. However, electrostatic interactions often cause deviations from purely hard-sphere interactions; in low dielectric medium this is particularly challenging to control as charge disassociation is poorly understood [24].

In this chapter, we describe the high-yield synthesis of a colloidal model system that enables previously inaccessible experiments, such as that of mixed charge systems [53, 54]. Using dispersion polymerization, we produce monodispersed latex particles of a random copolymer of poly-trifluoroethyl methacrylate (PFEMA) and poly-\textit{tert}-butyl methacrylate (PtBMA), which allow the simultaneous matching of the refractive index and density with a binary mixture of non-volatile and polar fluids. Additionally, we prepare particles of the same copolymer containing a fluorescent core and a non-fluorescent shell, enhancing the accuracy of particle tracking in densely-packed 3D confocal experiments [32, 55]. Moreover, we show that the interac-
Chapter 3: Synthesis of refractive index matched colloids in polar solvents

Figure 3.1: Schematic representation of the synthesis and surface modification of copolymer colloids by dispersion polymerization and ATRP.

Interparticle interactions are thereby altered from hard-sphere like to long-range repulsive through changes in the ionic strength of the high dielectric suspending fluid. This exquisite control allows for the growth of cationic or anionic brushes with similar surface charge densities; mixtures of these oppositely charged colloids co-assemble through electrostatic interactions into colloidal gels.

Common drawbacks for the colloidal model systems are a direct consequence of the material composing the particles. Inorganic particles, such as silica, have high densities hindering density matching, while organic latex particles composed of different polymers, such as styrenics or acrylates, typically have undesirably high refractive indices and/or low glass transition temperatures; therefore the focus of this work became methacrylates with relatively high glass transition temperatures and relatively low refractive indices respectively. Dispersion polymerization of the simplest methacrylate, methyl methacrylate, using the polymeric stabilizer poly(vinyl pyrrolidone) (PVP) is extensively documented. We found a binary mixture of
Table 3.1: Composition of PVP dispersion polymerization mixtures, all volumes in milliliters. The following are held constant: volume ratio of FEMA:tBMA at 28:72, AIBN (1wt% to monomer), steric stabilizer PVP (4wt% to solvent), reaction time (16 hrs), and temperature (55°C). Average particle diameters from SEM and Optical microscopy are listed in microns; CV, the coefficient of variation, is defined as $\sigma/\langle a \rangle$.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Monomer</th>
<th>Inimer</th>
<th>Methanol</th>
<th>Cosolvent</th>
<th>SEM</th>
<th>Optical CV</th>
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</thead>
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<td>10.0 (water)</td>
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<td>3.75 (FM)</td>
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Thioglycerol and formamide, FM, matches both the density and refractive index of poly-methylmethacrylate, PMMA [$\rho = 1.19g/ml$, $n = 1.492$]\(^{58}\). Although these PMMA particles are stable in this polar mixture for at least one year, confocal microscopy measurements indicate that these colloids do not behave like repulsive hard-spheres but are weakly attractive. We speculate that this attraction is due to thioglycerol being a poor solvent for the steric stabilizer, PVP. To circumvent this issue, we explore particles composed of a copolymer of two methacrylates. We will show the ability to polymerize particles, create fluorescent core/shell particles, simultaneously match refractive index and density, and modify the particle surface which directly controls the particle interactions.
3.1 Synthesis of copolymer colloids

Fluorinated methacrylate polymers, such as PFEMA, have relatively low refractive indices \((n \leq 1.415)\), yet a very large density \((\rho \sim 1.538g/ml)\). Conversely, conventional methacrylate polymers have densities that decreases with the length of the alkyl group \((\rho \sim \text{methyl methacrylate} > \text{ethyl methacrylate} > \text{tert-butyl methacrylate})\), but exhibit relatively high refractive indices \((n_{PMMA} \approx 1.495)\). Combining these two types of monomers at different molar ratios yields a copolymer with easily tuned density and refractive index. Here we choose a combination of FEMA and tBMA. Homopolymers of each exhibit the following properties: PFEMA \([\rho = 1.53g/ml, n = 1.4185]\) and PtBMA \([\rho = 1.022g/ml, n = 1.4630]\). At a volumetric ratio of 28:72, PFEMA:PtBMA, particles have a relatively low density, \(\rho = 1.16g/ml\), refractive index, \(n = 1.452\), and high glass transition temperature, \(T_g \sim 86^\circ C\). The dispersion copolymerization of FEMA and tBMA yields colloids with a very low polydispersity, typically CV\(\leq 5\%\) (Table 3.1 & 3.2). We control the particle size from \(a \sim 0.55\mu m \sim 8\mu m\) by simply changing the type and amount of cosolvent during PVP dispersion polymerization and monomer volume fraction during charged dispersion polymerization, discussed in the next section (Fig.3.7)[Sec. 3.7.2, 3.7.4]. Modifications to the polymerization temperature, dispersant concentration, and initiator concentration could yield a wider range of particle diameters but are not explored in this study[57]. The chosen comonomer ratio is specific to the final suspending fluid discussed below.
Chapter 3: Synthesis of refractive index matched colloids in polar solvents

Figure 3.2: Core-shell particles. (a) SEM of core particles, $a \sim 710 nm$, batch #5 (b) SEM of final particles, $a \sim 1.8 \mu m$, batch #3 (c) 2D confocal microscopy image of the fluorescent core with shell outlines (dotted lines) determined by simultaneous bright-field microscopy, not shown. The single small particle seen in (b) is a core from (a) that was not encapsulated during shell polymerization. Scale bar in all images is 2$\mu m$.

3.2 Core-shell particles

Many colloidal experiments use confocal microscopy to directly image fluorescent particles in 3D. In most cases, interesting behavior in colloidal suspensions such as crystallization or vitrification occurs at relatively high volume fractions, $\phi \geq 30\%$. As a consequence, particles are spatially close together making accurate locating of the particle centers from confocal microscopy difficult due to overlapping fluorescent regions, especially as the particle size approaches the diffraction limit, $\approx 300 nm$ for confocal experiments. We resolve this difficulty by using colloids with a fluorescent core and a non-fluorescent shell yielding well separated particle centers, eliminating areas of overlapping fluorescence.

We prepare core-shell particles by seeded-dispersion polymerization in the presence of cross-linked fluorescent core particles. To synthesize core particles, we use a modified dispersion polymerization where a charged co-monomer is incorporated into
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the polymer network, thereby electrostatically stabilizing the final particle. This approach yields highly monodispersed particles with a clean surface free of dispersant or surfactant [59]. Moreover, we are able to synthesize single-step crosslinked particles by adding up to 2vol% ethylene glycol dimethacrylate (EGDMA), while maintaining excellent monodispersity and sphericity (Fig. 3.2a, Table 3.2). Polymerizations performed at volume fractions of monomer >5vol% and cross-linker >2vol% produced an undesirably large number of particle dimers and trimers.

To prevent leaching of the fluorophore into the shell during the second growth step, we incorporate three new polymerizable fluorophores into the crosslinked core particle; this addition has no discernible effect on particle size, monodispersity or sphericity, a common problem with other fluorescent particle polymerization methods [32]. Two reactive fluorescent monomers, rhodamine-B labeled styrene and 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole based methacrylate are extensively used to fluorescently label non-aqueous PMMA colloids [48, 49, 60, 32, 55, 33]. Here we synthesize three new polymerizable fluorophores, to extend the excitation and emission range and to provide higher photostability; (i) coumarin-methacrylate (ex:446nm/em:490nm), (ii) pyrromethene-methacrylate (ex:514m/em:532nm) and (iii) rhodamineB-methacrylate (ex:543nm/em:605nm) [Sec. 3.7.3]. Each of these fluorophores is confirmed to be successfully incorporated into the core particles by dissolving the particle in excess THF, centrifuging, and measuring the fluorescence intensity in the supernatant compared to the sediment.

The non-fluorescent shell is formed by a seeded dispersion polymerization in the presence of cross-linked fluorescently labeled core particles. The cosolvent ratio chosen
determines the maximum particle size possible; the desired particle size must always be small than this maximum or secondary nuclei will generate unwanted, uncored particles. This is accomplished by knowing the volume fraction of cores and the total volume of monomer during the shell polymerization assuming that nearly all cores are incorporated (>98%); the result is monodispersed core-shell particles as seen in Fig. 3.2. Unincorporated core particles are removed by gentle centrifugation. By restricting fluorescence to only the core of the final particle, the visible center to center distance between adjacent colloids is increased by twice the shell thickness, as illustrated in Fig. 3.2c.
3.3 Surface modification

After particle formation, we use surface-initiated Atom Transfer Radical Polymerization (ATRP) to control the surface chemistry of colloidal particles[56]. With ATRP a nearly infinite number of polymer types may be grown from the surface of the particles, allowing the surface chemistry to be tailored with a great degree of flexibility. ATRP is capable of adding cationic changes, anionic charges, lower critical solution temperature or upper critical solution temperature properties. To perform an ATRP, we employ two different inimers which are randomly incorporated into the particle during dispersion polymerization[61]. No significant difference in particle diameter is seen between inimers (Fig.3.7). For some of the dispersion polymerization, a steric stabilizing dispersant (PVP K30, \( c^* \sim 4 \text{wt}\% \)) is used in the reaction at or near the polymer overlap concentration, \( c^* \), which coats and stabilizes the final particle surface. Our initial concern with using ATRP to modify the surface after particle formation is this dense dispersant layer might inhibit modification. To confirm that surface polymerization is successful, we grow a brush of a fluorescent monomer from the surface (Fig.3.3). Although the fluorescent brush thickness is well below the diffraction limit, a fluorescent halo is clearly distinguishable around each particle; indicating surface modification despite the presence of a steric layer.

To control the interparticle potential, we adjust the surface charge density using ATRP electrosteric stabilization. The efficiency and control (polydispersity) during an ATRP reaction depends on several factors: ligand, copper concentration, temperature, and solvent composition. We note that a aqueous mixture of formamide, FM, in conjunction with a commercially available ATRP ligand, HMTETA, leads to a signif-
significantly higher reactivity compared to aqueous mixtures of alcohols, such as methanol or ethanol, or to pure water [Sec.3.7.5]. Reaction conditions are optimized for producing highly charged particles within a reasonable amount of time, ~6hrs, by adjusting the copper(I) to copper(II) ratio to 1:1 by mole; a sacrificial initiator is employed to control the degree of polymerization of the growing brush as it is unknown how many surface inimer molecules are accessible for polymerization on the particle. We use acrylamide monomers for the surface modification instead of methacrylates as they are more soluble in polar solvents and exhibit lower reactivity[62]; this enhances the control over the polymerization rate. To illustrate this control, we prepare brushes of a copolymer of a neutral, DMA, and anionic, SPAm, acrylamides at different molar ratios of the two monomers. The surface charge density of these particles is calculated using measured ζ-potential values by the following empirical relation[63]:

$$\tilde{Z} = \epsilon \epsilon_0 kT e \kappa \left[2 \sinh \left(\frac{\psi}{2}\right) + 4 \kappa a \tanh \left(\frac{\psi}{4}\right)\right]$$  \hspace{1cm} (3.1)

where $\tilde{Z}$ is the surface charge density, $\epsilon$ is the dielectric constant of the suspending fluid (\(\sim 82\)), $\epsilon_0$ is vacuum permittivity, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $e$ is the elementary charge, $\kappa$ is the inverse Debye screening length, and $\psi = \left(\frac{\zeta e}{kT}\right)$. By adjusting the ratio of neutral to charged monomer, we control the final charge density on the particles which is not possible with other colloidal systems as seen in Fig.3.4.
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Figure 3.4: Calculated surface charge density (Eq. 3.1 after ATRP with different molar ratios of charged to neutral monomer for identical reaction times. Inset: \( \zeta \) potential values measured in 10mM TRIS, pH 7.5.

Figure 3.5: (a) 2D x-y confocal microscopy slices of a Wigner crystal; batch #2 particles at \( \phi \sim 40\% \) in deionized, refractive index and density matched solution. Scale bar is 20\( \mu m \). Inset: higher magnification, with a scale bar of 2\( \mu m \). (b) x-z confocal microscope slice of the Wigner crystal. Scale bar is 5\( \mu m \). (c) 3D particle reconstruction from particle locations; distances in microns, starting at 15\( \mu m \) from the coverslip.
3.4 Refractive index and density matching

For electrostatic experiments utilizing confocal microscopy, the suspending fluid for these copolymer particles should meet certain experimental criteria: non-volatile, high dielectric constant, and match both the refractive index and density of the colloids. Additionally, the fluid must not swell or soften the particle, which causes gradual degradation of the particles, changes in volume fraction and leaking of the fluorophore from the particle. Moreover, the suspensions must be highly stable in the suspending fluid, showing no signs of aggregation or fluorophore deterioration over extended periods of storage.

We accomplish all of the above by choosing a specific comonomer ratio in the particle, such that mixtures of formamide (FM) and sulfolane (SF) match both the refractive index and density of the colloids. At the same time, this solvent mixture is inert and a poor solvent for the copolymer that composes the colloids. A 72:28 FM:SF volumetric ratio ($\rho = 1.16g/ml$, $n = 1.452$) does not plasticize the particles; inferred by observing no fluorophore leaking into the suspending fluid over 36 months while matching both the refractive index and density of the colloidal particles. Interestingly, this mixture of solvents has an estimated dielectric constant of $\epsilon \sim 82$, nearly the same as that of water[64].

3.5 Interparticle interaction

The interactions between these electrosterically stabilized colloids is also tunable by changing the suspending fluid conditions. We perform confocal microscopy experi-
ments on a single batch of 1.4μm particles, which are surface-modified with an anionic brush (Sec. 3.7.5). By controlling the ionic strength in the suspending fluid, the interaction potential changes from hard-sphere like to a soft and long-ranged electrostatic repulsion. The Debye screening length should be larger for high dielectric solvents like water or formamide (ε ~ 80) compared to low dielectric solvents for identical ionic strengths as $\kappa^{-1} \propto \sqrt{\epsilon I}$, where $\epsilon$ is the dielectric constant of the suspending fluid and $I$ is the ionic strength. However, in practice, polar solvents always have relatively high inherent ionic strengths due to impurities or through self-ionization; this is partially solved by deionizing the fluids through extensive treatment with ion exchange resins. The conductivity of formamide as received is 68μS/cm and that of sulfolane 6.6μS/cm. After deionization with a mixed bed ion exchange resins, the conductivity decreases to 1.0μS/cm and 0.23μS/cm, respectively. To demonstrate that particles suspended in this deionized solvent exhibit a long-ranged repulsive potential, colloids (batch #2, $\zeta$ ~ -64mV, 2r~1.4μm) are washed twice with deionized solvents then refractive index and density matched by fine-tuning the ratio of these suspending fluids. The volume fraction is initially determined by resuspension from a known volume of random close packed sediment ($\phi$ ≈ 64%) with a known solvent volume. Volume fractions are verified by particle counting and by solvent evaporation with thermogravimetric analysis. The suspension (batch #2, $\phi$ ~ 40 ± 2%) is tumbled for several days in the presence of ion exchange resins. The result is a colloidal Wigner crystal formed at a significantly lower volume fraction than the onset of fluid-crystal coexistence for hard-spheres ($\phi$ ~ 48%)[21](Fig.3.5). Individual particles diffuse as the confocal scans in Z causing the particles to appear aspherical as seen in
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Figure 3.6: 3D radial distribution function, $g(r)$, normalized by particle radius, $a$ from SEM. ($\circ$) a hard-sphere potential ($\phi \sim 40\%$, 50mM NaCl); (solid line) near perfect hard-sphere behavior calculated using the Percus-Yevick approximation. Inset: (●) Wigner crystal ($\phi \sim 40\%$, 0mM NaCl) seen in Fig. 3.5; dashed lines are hexagonal close packed positions. The nearest neighbor peak is shifted to $r/a \sim 1.24$ indicative of a long ranged repulsive interaction potential.

Fig.3.5b; Wigner crystals can have extremely small elastic moduli, $\ll 1\text{Pa}$, yielding large particle displacements without order rearrangement [65]. We are also able to locate individual particle centers deep into the sample due to the refractive index matching of the suspending medium and particles (Fig.3.5c). This demonstrates our ability to create a highly repulsive, soft interparticle potential in this polar medium.

Finally, we add 50mM NaCl to the same suspension, to screen all electrostatic repulsion as the Debye screening length, $\kappa^{-1}$, decreases to $\approx 1\text{nm}$ yielding a repulsive hard-sphere like potential; $\phi \sim 40$ is below the onset for hard-sphere fluid-crystal coexistence and should yield only a colloid fluid [21]. To confirm that we do indeed have a fluid, we compute the radial distribution function, $g(r)$, from 3D particle positions obtained through confocal microscopy (Fig.3.6). The pair-correlation function is well described by the Percus-Yevick approximation using a volume fraction $\phi \sim 42\%$ and
particle radius $r \sim 0.74\mu m$, both values well within experimental uncertainty, confirming the nearly hard-sphere behavior of this dispersion with small screening lengths.

### 3.6 Chapter summary

Within this single batch of colloidal particles, we are able to alter the interparticle potential drastically by simply adding salt. We fully understand this change as the added salt readily disassociates and screens surface charges due to the highly polarity of the dispersed phase; by contrast such insight in low dielectric systems is challenging [24]. We have presented extensive synthesis details of this new colloidal system comprised of copolymer latex particles with tunable surface potentials that are refractive index and density matched. Particularly well suited for microscopy and rheology, these colloids possess many desirable chemical and physical properties while lacking many of the experimental constraints found in other model colloidal systems.

### 3.7 Experimental for this chapter

All materials are purchased from Sigma-Aldrich and used as received, unless otherwise noted.

#### 3.7.1 Inimer preparation

The term *inimer* has been used to describe an *initiator* for Atomic Transfer Radical Polymerization that is also a polymerizable *monomer* [61]. Here, we prepare 2 different types of inimers: 2-(2-bromoisobutyryloxy) ethyl acrylate and 2-
(2-bromoisobutyryloxy) ethyl methacrylate. To synthesize each, α-bromoisobutyryl bromide (0.35 moles) and dichloromethane (50 ml) are added drop wise over 1 hour to a cooled solution of 2-hydroxyethyl acrylate (0.35 moles) for the acrylate-inimer, or 2-hydroxyethyl methacrylate for the methacrylate-inimer in triethylamine (0.38 moles), and dichloromethane (250 ml). After drip addition, the reaction is allowed to proceed for 12 additional hours at room temperature. A white precipitate (triethylamine-HBr) is formed, and removed by filtration. The solvent is evaporated, during which more white precipitate is formed and filtered off. The solution is washed three times with deionized water (300 ml) and the lower organic phase recovered. This product is dried by addition of anhydrous Mg$_2$SO$_4$ (3 g), and decolorizing carbon (2 g), and passed over a silica gel bed (200 mesh); this procedure is repeated twice. The result is a pale yellow colored oil. Acrylate-inimer: yield 54.2 g (~74%); methacrylate-inimer: yield 58.4 g (~82%).

### 3.7.2 Dispersion polymerization using PVP stabilizer

Most particle polymerizations using PVP as the steric stabilizer are conducted in a 200 ml round bottom flask tumbled in a heated glycerol bath by an overhead stirrer. Typical polymerization mixtures are found in Table 3.1. A dispersion reaction proceeds as follows: methanol (90.0 ml), deionized water (10.0 ml), 2,2,2-trifluoroethyl methacrylate (2.8 ml, FEMA, SynQuest Laboratories), tert-butyl methacrylate (7.2 ml, tBMA, TCI America) at a ratio of 28:72 by volume, polyvinylpyrrolidone (4.0 g, PVP K30), inimer (0.5 ml) and 0.100 g of 2,2-Azobis(2-methylpropionitrile) (AIBN) are added to the reaction flask (see Table 3.1). The flask is brought under vacuum and
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subsequently purged with nitrogen, which is repeated several times to obtain oxygen-free conditions. The reaction mixture is then tumbled at $\approx 75$ rpm in a glycerol bath at $55^\circ$C for 16 hours. The resulting particles are washed by repeated centrifugation and redispersion in a 1:1 water-methanol mixture. Polymerizations are invariant to total reaction volume; reaction volumes up to 1000 ml have been conducted with no changes to the final particle size and polydispersity.

3.7.3 Fluorescent monomers

We synthesize three new fluorescent monomers: coumarin-methacrylate, rhodamineB-methacrylate and pyrromethene-methacrylate. First by Steglich esterification\textsuperscript{[66]}: coumarin 519 (1.75mmoles, Exciton), dichloromethane (65ml), 4-(dimethylamino)pyridine (0.52mmoles) and 2-hydroxyethyl methacrylate (7.0mmoles) are added to a 200ml flask. While on ice, N,N-dicyclohexylcarbodiimide (2.62mmoles) is added and the reaction proceeds for 3 hours at room temperature. The product is then washed with 0.5M hydrochloric acid (2X), followed by saturated NaHCO\textsubscript{3} (2X), dried with anhydrous Mg\textsubscript{2}SO\textsubscript{4} (3 g) which is filtered off, and excess dichloromethane removed by rotary evaporation. The dry product coumarin-methacrylate (390mg, $\sim 70\%$ yield) is dissolved in methanol at $\sim 2\text{wt}\%$ and stored at $4^\circ$C.

Second by base-catalyzed nucleophilic addition; rhodamine B (3.1mmoles), toluene (150ml), glycidyl methacrylate (3.25mmoles), N,N-dimethyldodecylamine (0.15mmoles) and tert-butyl catechol (0.06mmoles) are added to a 250ml flask and refluxed at $115^\circ$C for 2 days. The reaction is cooled, filtered over glass wool and toluene removed by rotary evaporation. The cationic monomer (1.10g, $\sim 73\%$) is stored in methanol at
Lastly to prepare pyrromethene-methacrylate, a boron-trifluoride mediated reaction is followed by Steglich esterification. A pyrromethene (BODIPY) derivative with a carboxylic functionality is first synthesized\cite{67}; glutaric anhydride (8.12mmoles), dry dichloromethane (100ml), 2,4-dimethyl-3-ethyl pyrrole (16.23mmoles) and boron trifluoride diethyl etherate (10.83mmoles) are consecutively added to a 200ml round bottom and refluxed at 50°C for 5 hours. The reaction is cooled to room temperature and under nitrogen, boron trifluoride diethyl etherate (54mmoles) and triethylamine (41mmoles) are added. The reaction is stirred overnight, washed with DI water (200ml, 2X), dried with Mg$_2$SO$_4$ and excess dichloromethane evaporated. The dark red oil product is passed over a silica gel column (2:1 hexane/ethyl acetate by volume) giving 420mg of solid pyrromethene-butyric acid (yield $\sim$17%).

Esterification proceeds with pyrromethene-butyric acid (1.0mmole), dichloromethane (40ml), 4-(dimethylamino)pyridine (0.353mmoles) and 2-hydroxyethyl methacrylate (4.2mmoles) added to a 100ml flask. On ice, N,N-dicyclohexylcarbodiimide (1.57mmoles) is added and the reaction allowed to proceed for 12 hours. The reaction is cleaned following a similar protocol as previous esterification and stored in methanol at $\sim$2wt% and stored at 4°C.

### 3.7.4 Dispersion polymerization using SPMA stabilizer

Particles polymerizations using a charged monomer stabilizer, 3-sulfopropyl methacrylate (SPMA) are conducted in a 200ml round bottom flask equipped with a reflux condenser. Typical polymerization mixtures are found in Table 3.2. These parti-
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Figure 3.7: (a) PVP stabilized particle diameters with changes in co-solvent and inimer type, see Table 3.1. • H$_2$O, no inimer; ♦ H$_2$O, acrylate inimer; ● H$_2$O, methacrylate inimer; ▼ formamide, acrylate inimer; ▲ formamide, methacrylate inimer. (b) SPMA stabilized particle diameters with cosolvent, H$_2$O, volume varied along with total monomer volume fraction, see Table 3.2. • 15vol% monomer; ■ 12.5vol% monomer; ◆ 10vol% monomer; ▼ 5vol% monomer. Reaction compositions within shaded regions yield only polymerized coagulum.
Table 3.2: Composition of SPMA dispersion polymerization mixtures, all values in milliliters. The following are held constant: volume ratio of FEMA:tBMA at 28:72, AIBN (1wt% to monomer), charged monomer (SPMA, 1wt% to monomer), acrylate inimer (2vol% to monomer), reaction time (4 hrs), and temperature (80°C). Average particle diameters from SEM are listed in microns.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Monomer</th>
<th>Methanol</th>
<th>Water</th>
<th>EGDMA</th>
<th>Fluor. Monomer</th>
<th>SEM</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.35</td>
<td>80.0</td>
<td>22.0</td>
<td>0.107</td>
<td>1.0</td>
<td>0.710</td>
<td>0.02</td>
</tr>
<tr>
<td>6</td>
<td>5.35</td>
<td>85.0</td>
<td>17.0</td>
<td>0.107</td>
<td>1.0</td>
<td>0.812</td>
<td>0.02</td>
</tr>
<tr>
<td>7</td>
<td>5.35</td>
<td>78.0</td>
<td>28.0</td>
<td>0.107</td>
<td>1.0</td>
<td>0.550</td>
<td>0.01</td>
</tr>
<tr>
<td>8</td>
<td>16.3</td>
<td>80.0</td>
<td>22.0</td>
<td>0.107</td>
<td>1.0</td>
<td>1.100</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Cores may also serve as crosslinked core for core/shell particles. A polymerization reaction proceeds as follows: methanol (80.0ml), deionized water (22.0ml), 2,2,2-trifluoroethyl methacrylate (1.45ml), tert-butyl methacrylate (3.9ml), SPMA potassium salt (0.055g), acrylate inimer (0.100ml, 2vol% to monomer), ethylene glycol dimethacrylate (0.107g, 2vol% to monomer), fluorescent monomer solution (1.0ml, 2wt% in methanol Sec.3.7.3) and AIBN (0.055g) are added to the reaction flask. The reaction flask is then heated to reflux, without degassing, at ~80°C for 5 hours. After completion, the particles are washed by repeated centrifugation and redispersion (5X) in a 1:1 water-methanol mixture. Successful fluorophore incorporation is verified by repeated centrifugal washing of the cross-linked particles in THF, a good solvent for the polymer, and comparing the fluorescence intensity in the supernatant to the sediment.
3.7.5 Surface functionalization

The inimer that is copolymerized during the dispersion polymerization [Sec. 3.7.2, 3.7.4] allows for the use of atom transfer radical polymerization (ATRP) to directly grow a polymer from the surface of the colloid\[56\]. To control the degree of polymerization of the growing polymer, a sacrificial ATRP initiator is added to the solution, assumed to be large excess of the available surface inimer molecules \[68\]. This sacrificial initiator, \textit{PEGini}, is synthesized identically to the acrylate inimer [Sec. 3.7.1] exchanging 2-hydroxyethyl acrylate for poly(ethylene glycol) methyl ether, \(M_n = 550\). A typical surface-modification proceeds as follows: formamide (FM, 32 ml), water (26 ml), PEGini (1.25 ml, 2.26 mmoles), 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (SPAm, 10.1 mmoles, 50 wt\% in H\(_2\)O), dimethylacrylamide (DMA, 47.1 mmoles), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 2.38 mmoles), Cu(II)Cl\(_2\) (1.13 mmoles) are added to a 200 ml flask containing the particle suspension (65 ml, 25 vol\% solids, in 2:1 H\(_2\)O:FM). The molar ratio between monomer : PEGini : copper : ligand is [25:1:1:1.05]. The suspension is bubbled with nitrogen or argon for at least 20 minutes to remove dissolved oxygen, then 1.13 mmoles of Cu(I)Cl is added to the flask to initiate the polymerization and tumbled for several hours (≥6 hrs). A fluorescently-labelled surface polymer brush is prepared by first reacting fluorescein isothiocyanate (0.08 mmoles) with N-(3-aminopropyl) methacrylamide hydrochloride (0.28 mmoles, Polysciences) in 2 ml of formamide at room temperature for 24 hrs. This fluorescent monomer is then polymerized from the particle surface using 3:1 by mass of 2,2'-bipyridyl:Cu(II)Br in 2:1 by volume FM:H\(_2\)O. The reaction is initiated with 5 mg of ascorbic acid and allowed to proceed for 1 hour.
3.7.6 Fluorescent labeling of the particles

Particles that do not contain a fluorescent monomer are fluorescently labeled using boron-dipyrromethene, or BODIPY, derivatives[69]. These fluorophores are hydrophobic, extremely photostable and exhibit a high quantum efficiency $> 90\%$, resulting in highly fluorescent and photostable colloidal particles. The particle suspension is swollen with an aqueous miniemulsion formed by sonication of carbon tetrachloride (10 vol%), containing dissolved fluorophore (Pyrromethene 546 or 605, Exciton), stabilized by 1 wt% Brij35. The total carbon tetrachloride volume is 50vol% to that of particle solids. This miniemulsion is added to a suspension of particles and stirred for at least 24 hrs. Subsequently, nitrogen is blown over the solution at 50°C for at least 6 hrs to evaporate the plasticizer, carbon tetrachloride. Free dye and surfactant are removed by repeated centrifugation and redispersion in a 1:1 water-methanol mixture.

3.7.7 Index and density matching

Particles are washed into deionized FM, with a conductivity of $\sigma = 1.00 \mu S$. Deionized tetramethylsulfonone (SF, $\sigma = 0.23 \mu S$) is added drop wise to a particle suspension at a volume fraction of $\phi \sim 0.40$ until the sample is completely transparent as judged visually. Density matching is verified by centrifuging the dispersion at 3000g for 6 hours. The suspending fluid mixture is adjusted until no sedimentation or creaming is observed. By synthesizing the colloids from a specific volumetric ratio of monomers (FEMA:tBMA, 28:72), both refractive index and density are simultaneously matched with a mixture of FM and SF at approximately 72:28 by volume. The
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final suspending fluid mixture has an estimated dielectric constant of $\epsilon \sim 82^{[64]}$. Ion exchange resins (Dowex Marathon MR-3) are added to further deionize the suspending fluid mixture.

3.7.8 Particle characterization

From optical microscopy (Nikon, TE2000) and scanning electron microscopy (SEM, Zeiss Supra 55), we obtain the number-averaged particle diameters and polydispersity; coefficient of variation, $CV$, is defined here as the standard deviation over the mean particle size, $\sigma/\langle a \rangle$. Refractive index and density matched samples are allowed to equilibrate for several hours in sample chambers, after which 3D image stacks are recorded using a confocal microscope (Leica SP5). Radial distribution functions are calculated using particle locating algorithms$^{[70]}$. Zeta potentials are measured with a Malvern Zetasizer Nano ZS on dilute particle suspensions in 10mM PIPES buffer at pH 7.0. The glass transition temperature of the copolymer is measured with differential scanning calorimetry (TA Instruments, Q200).
Figure 3.8: Scanning electron microscopy (SEM) image of (a) batch #1, average diameter 1.4\(\mu m\) (b) batch #2, average diameter 1.8\(\mu m\). Scale bar in both images is 20\(\mu m\).
Chapter 4

Experiments of refractive index matched colloids in polar solvents

As we saw in the previous chapter, model colloids in high dielectric solvents offer an excellent avenue for studying electrostatic interaction in an environment where Coulombic forces are well understood, namely a high dielectric dispersed phase. This chapter will explore more experiments that utilize this system for both its charge control in the form of mixed charge interactions, and for its copolymer composition which permits a fine tuning of density difference while still behaving as electrosteric hard-spheres. There are 4 projects that I will briefly discuss; greater detail may be found in the corresponding publications which at the time of this thesis’ publication are still forthcoming. They are briefly, cycling mixed charge attraction using salt [54], oppositely charged gelation [53], crystal-crystal grain boundaries, and lastly, crystal-liquid surface stiffness similar to [71].
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4.1 Reversible assembly of oppositely charged hairy colloids in water

We show an experimental study of the fully reversible assembly of oppositely charged colloidal particles in aqueous solutions: polystyrene colloids (not index matched to the solution) are charged by a grafted polyelectrolyte brush on their surface and stabilized at all salt concentrations by a neutral adsorbed polymer layer as seen in Fig. 4.1.

Below a critical salt concentration oppositely charged colloids form clusters and gels with a fractal nature. Above the critical salt concentration no aggregation takes place, due to the stabilizing neutral adsorbed polymer. Moreover, the aggregated structures are fully reversible and can be redispersed by simply increasing the salt concentration above the critical concentration as seen in Fig. 4.2.

We confirm that time-dependent interaction forces are at the basis of the formation of clusters in the present system by atomic force microscopy measurements as
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Figure 4.2: Mixtures of oppositely charged PS particles with a diameter of 1.1µm with either a cationic (colored red) or an anionic brush (colored green) aggregate at an overall volume fraction of 2.5%. (a) Completely aggregated dispersion at low salt concentrations, (b) partly aggregated dispersion at intermediate salt concentration, (c) homogeneous dispersion at high salt concentrations. (d) A confocal image of a gel at $\phi = 2.5\%$ and 1.5 M salt, 10 min after mixing. The inset is a zoom-in. (e) A confocal image of the dispersion in c. (f) Scattered intensity of the particle suspension after settling, corrected for refractive index ($n$) and overall particle concentration and normalized by the scattered intensity at 3.0 M KCl ($I_0$), as a function of salt concentration. The arrows refer to three examples of states of the system as shown in (a-c). The gray area indicates the critical salt region. (g) Scattered intensity of the particle suspension as in (f) when the salt concentration is switched repeatedly from 1.9 M to 0.35 M KCl (i.e. between the situation as indicated in (c and a) respectively). The time difference between cycle 1 and 2 is roughly 10 min, between cycle 8 and 9 roughly 4 h. The scale bars in d and e are 10µm.
a function of salt concentration and contact time as shown in Fig. 4.3. The force measurements show that the attraction between particles strengthens in time due to inter-penetration of the polymer brushes, driven by polyelectrolyte complexation[72]. These particles are a promising step toward a reversible and controlled self-assembling system in water, using colloidal particles as building blocks.

This work was performed with collaborators from Wageningen University.

Publication from this work:
Evan Sprujit and Henriette E. Bakker and Thomas E. Kodger and Joris Sprakel and Martien A. Cohen Stuart and Jasper van der Gucht, Soft Matter, 2011, 7, 8281 [54]

4.2 Gelation of oppositely charged particles

Here we utilize the unique features of this particle system; charge control and refractive index and density matching allowing 3D confocal microscopy to locate each charged particle. While colloidal gelation has been extensively studied for the case of purely attractive systems, little is understood about how colloidal gelation is affected by the presence of repulsive interactions. Here we demonstrate the gelation of a binary system of oppositely charged colloids, in which repulsive interactions compete with attractive interactions as shown in Fig. 4.4.

We observe that gelation is controlled by varying the total volume fraction, the interaction strength, and the new tuning parameter of the mixing ratio of the two particle types, and present a state diagram of gelation along all these phase-space coordinates as shown in Fig. 4.5. Contrary to commonly studied purely attractive
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Figure 4.3: Averaged rupture forces of the interaction between anionic and cationic colloids with a diameter of 3.5µm as a function of the time of contact between the colloids. 100 individual rupture events have been binned into 100 ms bins between 0 and 10 s and in 1000 ms bins for longer times. The solid lines are logarithmic fits to the data. The numbered labels indicate the concentration of KCl in each set of experiments. The inset is a zoom-in of the first 8 s.
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Figure 4.4: Confocal images of binary mixtures of oppositely charged colloids. Negatively charged particles are shown in yellow, and positively charged particles in magenta. Interaction strength decreases in (a-c), exhibiting the transition from a gel at high interaction strengths to a fluid at low interaction strengths. Mixing ratio increases in (d-f), exhibiting the same transition accessed using a different tuning parameter. (a) Mixing ratio of anions to cations $R = 1$, added salt concentration $c = 100$ mM; (b) $R = 1$, $c = 130$ mM; (c) $R = 1$, $c = 150$ mM; (d) $R = 4$, $c = 100$ mM; (e) $R = 6$, $c = 100$ mM; (f) $R = 8$, $c = 100$ mM. $\phi_{\text{tot}} \sim 0.1$ and scale bar is 20 m for all samples.
Figure 4.5: State diagram for the gel transition of a symmetrically mixed binary charged system; fluid samples are denoted by triangles, and gel samples by circles. The square point could not be identified as gel or fluid using the mean-square displacement criterion. The line is drawn as a guide to the eye. (b) One-dimensional mean square displacement curves for samples at several salt concentrations and $\phi_{tot} \sim 0.05$, showing the change from arrested to diffusive behavior. From bottom to top, $c = 100$ mM, 120 mM, 130 mM, 140 mM, and 150 mM. Inset: the same data on a loglog plot. (c) Frequency-sweep measurements for the strongest gels; solid symbols give the storage modulus $G'$, while open symbols give the loss modulus $G''$. For clarity, only two examples of the loss modulus are shown. $c = 60$ mM (circles), 80 mM (down-triangles), 90 mM (squares), 100 mM (diamonds), 110 mM (up-triangles), and 120 mM (hexagons). $\phi_{tot} \sim 0.2$ and $\gamma = 0.1\%$ for all samples.
Figure 4.6: Distribution of the number of positively charged contacts of negatively charged particles (a, c and e), and negatively charged contacts of positively charged particles (b, d and f) as the mixing ratio $R$ is changed. (a-b): $c = 100$ mM; (c-d): $c = 110$ mM; (e-f): $c = 120$ mM. Note that the trends in a, c, and e are similar to that in Fig. 4a, while in b, d, and f, there seems to be an approach to a saturated distribution at the highest asymmetry. All samples at $\phi_{\text{tot}} \sim 0.1$. 

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gels, in which weakly quenched gels are more compact and less tenuous, we find that particles in these binary gels form fewer contacts and the gels become more tenuous as we approach the gel point. This suggests that a different mechanism governs gel formation and ultimate structure in binary gelation: particles are unable to form additional favorable contacts through rearrangements, due to the competition of repulsive interactions between similarly charged colloids and attractive interactions between oppositely charged colloids as shown in Fig.4.6.

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4.3 Interfacial tension

In the following two subsection, the system will be used as model hard-spheres. The short ranged electrosteric interparticle repulsive potential between similarly charged colloids is nearly hard-sphere like at high salt concentration as shown in Chapter 3. Crucial to these two projects is the ability to finely tune the density difference between the particle and continuous phase; each of these projects relies on small $\Delta \rho \sim 5-50kg/m^3$. Here we will utilize this small density difference, fine temperature control, and experimental patience to form a sample with a well defined and small volume fraction gradient in the gravitational directions. This experimental setup combined with a horizontal confocal, as shown in Chapter 9, allows us to directly observe the transition from liquid to crystal with unprecedented control in $\phi$.  

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4.3.1 Crystal-liquid surface tension

Using confocal microscopy, a previous study has observed capillary fluctuations at a liquid-crystal interfaces. By sedimenting hard-sphere particles onto the three high-symmetry planes of the FCC crystal system $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$, the surface stiffness, $\tilde{\gamma}$ is calculated using the the slope of the inverse squared Fourier components, such that,

$$\langle |h_2|q \rangle \approx k_B T \tilde{\gamma}(\theta)q^2$$

where $h$ is the height of the identified interface and $q$ is the in-plane wave vector.

Unlike simulation, the measured values were not sufficient to observe any anisotropy in $(110)$ surface stiffness; the most likely cause of this was the use of very heavy silica colloids. Specifically, the gravitation height was smaller that the actual thickness of the identified interfacial width.

Using the polymer latex particles discussed in Chapter 3, we duplicate these experiments, now with an order of magnitude decrease in $\Delta \rho$ compared to silica; the gravitational height in this system is $k_B T/mg \approx 1.5\sigma$, where $\sigma = 1.55 \mu m$ is the particle diameter. Despite these lighter colloids being much more susceptible to temperature fluctuations and mechanical perturbations, we have successfully formed crystals in the three templated planes as shown in Figure 4.7. Each of these colloidal crystals is leveled on the confocal microscope, left in place to thermally and mechanically equilibrate for at least 24 hours prior to measurement. Local heating of the interface by the scanning laser is also observed and minimized by using very low laser powers, $< 0.3 mW$. By creating crystals that are at least $50 \mu m$ tall, we eliminate
any constraints imposed by the rigid template; however, observing deep into a colloidal sample at high $\phi$ requires the refractive index matching between the particle and dispersed phase to be nearly perfect. Additionally, by matching the refractive index of objective immersion fluid to the sample, we eliminate any loss of image contrast at large depths. To image, we use a modified silicone oil, Gelest (ALT-143) $n=1.445$, which matches the refractive index of the dispersed phase, formamide, and a glycerol immersion 63X objective with a correction collar which is adjusted for the thickness of the template fabricated from normal coverslip glass, $n=1.518$. Currently, this data is under analysis. This work is a collaboration with Sanne van Loenen of Peter Schall’s laboratory at the University of Amsterdam who performed this work as her master’s project and Emily Redston of the Spaepen Lab and of course Profs. Schall and Spaepen.
Figure 4.7: (a) XZ confocal slice of a ⟨110⟩ templated RHCP crystal in equilibrium with a colloidal liquid; the template is seen at the bottom of the image. The gravity direction is down. (b) XZ confocal slice of a ⟨111⟩ templated RHCP crystal; only shown is the crystal-liquid interface (c). XZ confocal slice of a ⟨100⟩ templated FCC crystal; only shown is the crystal-liquid interface.
4.3.2 Crystal-crystal interfaces

While electron microscopy has recently produced many stunning images of metallic surface and crystal growth, observing within the material is still impossible due to the inherent limitations of transmission electron microscopy. Colloidal particles provide an excellent analog to real metals, but on time and length scale that are experimentally accessible, while crucially, allowing true 3D observation not 3D interpretation from diffraction patterns. Highly monodispersed core-shell are slowly sedimented over several months and allowed to equilibrate at constant temperature. By observing perpendicular to the gravitational axis, these colloidal crystals are observed without disturbing the fragile equilibrium between pressure and crystal elasticity that has developed. Due to the slow crystal growth rate, the entire sample has only a few large crystals which span nearly 5mm across by 30mm in the settling direction. This provides only a limited number of crystal-crystal interfaces but these interfaces are nearly perfect with no defects and very few stacking faults. By measuring the instantaneous fluctuations of this interface through particle locating, we are able to measure the interfacial tension of such a boundary, which is otherwise unmeasurable. This work is a collaboration with Emily Redston of the Spaepen Lab, see Fig. 4.8 for raw and measured data.
Figure 4.8: (a) 2D slice from a 3D confocal image stack of a crystal-crystal interface. The gravity direction is to the left. (b) Computer rendering of only those colloidal particles identified to be interface particles from (a). Note, the large fluctuations in the vertical direction.
Chapter 5

Colloidal gels

5.1 Colloidal gel introduction

At sufficiently high volume fractions, colloids that interact through a long or short-range attraction form a gel \([16, 73]\), a percolated network structure arrested in a thermodynamically non-equilibrium state possessing a functional yield stress as shown microscopically in Fig. 5.1a. As such colloidal gels are not covalently crosslinked, they do not possess a true yield stress as found in polymeric gels. When a stress smaller than the functional yield stress is applied to the material, the initial response is elastic, but after some time the material can suddenly yield and start to flow \([5, 74]\); a phenomenon known as delayed yielding or delayed failure. Colloidal gels are encountered in drug delivery systems \([75]\), food products \([76]\), cosmetics, paints, coatings. The delayed yielding of colloidal gels subject to gravitational forces, known as delayed collapse, limits the shelf-life of these products \([4]\). Thus, their stability under loads is of direct interest. Gravity induces compression in the bulk...
and shear near adhesive vertical walls [77, 78]. Under gravitational load as well as in simple shear, the time delay before yielding decreases exponentially with stress [4, 5], indicating that a stress-dependent energy barrier governs failure at the particle-level [4]. However, this picture is complicated by the strand architecture, which has an order-of-magnitude effect on delay time [3]. To achieve predictive capability with a physical model, we must consider the full complexity of the system, that is to include the effects of thermal fluctuations and stresses at all levels of structure.

The creep response of colloidal gels typically displays three regimes: an initial elastic deformation, a subsequent primary creep regime where the creep rate decreases with strain and finally a catastrophic failure [3, 5, 74]. This behavior is found in weak [3] and strong colloidal gels [3, 5, 74] as well as in polymeric gels [79, 80]. Experiments indicate that the delay time $\tau$ decreases exponentially with applied shear stress $\sigma$ for strong gels of stearylated-silica particles in oil [5] and carbon black particles in oil [74]. This suggests the presence of an energy barrier that decreases linearly with applied stress [74]. A similar exponential scaling of delayed yielding time with stress is also observed for polymeric gels [79, 80]. Interestingly, if a preshear is applied to the colloidal gel, the delay time shows two distinct stress regimes. The delay time increases exponentially with decreasing stress, but with different exponential factors in the two regimes. This is observed for stearylated-silica particles suspended in dodecane and carbon black in tetradecane, which both form strong gels, and in a weak polystyrene particle gel with a depletion attraction [3]. The two regimes are attributed to the hierarchical architecture of particles and strands in conjunction with the stress-enhanced dissociation rate and association rate of colloid–colloid bonds [3].
In this chapter, we will further describe the theory and experiments for delayed yielding in colloidal gels under a static loading as published in [3, 81]. This theory relates the applied stress, parameters of colloidal interactions and strand structure to the delayed yielding time. The model emphasizes the importance of the gel strand structure, which can be modified by quench history [82] and flow history [83, 84]. We address how to control the strand structure to optimize material performance in delayed yielding by experimentally investigating the effects of preshear and quench rate on the delayed yielding time and interpret the results in light of our new model. This provides a crucial new understanding directly applicable to industrial processing of gel-based products.

5.2 Yielding at multiple length and time scales

Colloidal gels have different structural features at clearly separable length-scales. At the microscale, the attractive particles aggregate to form gel strands, at the mesoscale, gel strands form a percolated network structure and at the macroscale the gel is a homogeneous material. These levels of structure are visible in a confocal microscope image of a colloidal gel comprising 1.1 µm particles at a volume fraction \( \phi = 0.12 \) in formamide/sulfolane depleted by 50 mg/ml, 500 kDa dextran as shown in Fig.5.1a; this experimental system is described in Chapter 3. It has been previously shown that these hierarchical structures strongly affect the moduli of gels, suggesting that they may also be pivotal to other mechanical properties including the delayed failure[85].

To describe the delayed yielding of these hierarchically structured materials, we
Figure 5.1: (a) Representative confocal microscope image of a colloidal gel of volume fraction $\phi = 0.12$. Note the three levels of structure: particle-level, strand-level and homogeneous macroscopic level. (b) Schematic illustration of two simultaneously detached colloid–colloid bonds (striped particles) at the neck of a strand. (c) Illustration of broken strand with seven broken bonds
model the system at multiple scales. A *particle-level* model describes the stress-enhanced bond dissociation. A *strand-level* model considers the collective dissociation/association dynamics of bonds at the neck of a gel strand and yields the strand dissociation rate. A *macroscopic model* relates the macroscopically applied stress to the strand dissociation rate and predicts the degradation of the material before damage localization and macroscopic failure.

### 5.2.1 Particle-level model

A colloidal particle of the formed gel is trapped in a potential well resulting from interactions with its neighbors. Within this potential well, irregular forces caused by thermal fluctuations of the surrounding medium induce particle vibrations, which can lead to the dissociation of a colloid-colloid bond. By considering the diffusion equation for the density distribution of particles in a colloid-colloid interaction potential, the dissociation rate of bonds can be derived\cite{86}. When no external force is applied across the bond, the dissociation rate becomes

\[
k_D = \omega_0 \exp\left(-\frac{E_A}{k_B T}\right),
\]

where \(\omega_0\) is the attempt frequency, \(E_A\) is the depth of the potential well, \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature. The frequency \(\omega_0\) depends on the diffusivity of the particles and the shape and depth of the potential barrier\cite{86}. When a force \(f\) is applied across the weakly attractive bond, the energy barrier is lowered\cite{87} and the dissociation rate is modified, becoming\cite{88},

\[
k_D' = k_D \exp\left(\frac{f\delta}{k_B T}\right), \quad f\delta < E_A,
\]

(5.1)
where $\delta$ is the characteristic width of the interaction potential. Here, the work performed by the applied force is approximated by $f\delta$. This model for the kinetics of bond dissociation has been experimentally verified for weakly attractive molecular systems\cite{89}. It should be mentioned that applying a force across the colloid - colloid bond slightly modifies $\omega_0$\cite{90}. This effect is neglected in the present model.

### 5.2.2 Strand-level model

If the cross-section of a strand includes several particles, many dissociation events are required for a strand to break as shown in Fig.5.1b-c. Due to thermal fluctuations, bonds also reform at an association rate $k_A$, which is assumed to be independent of the applied stress. Since the thickness of a strand varies along its length, it is assumed that fracture will occur at an existing “neck”, the weakest point along its contour, that has a cross-section of $n$ bonds. The integer number of intact bonds at the neck is denoted by $j \in [0, n]$.

During the rupture of a single strand, we assume that the macroscopic stresses are constant; which is achieved experimentally in creep experiments. Even so, the force on the breaking strand may not be constant. When some of the bonds break at the neck of a *straight* strand, the tensile stiffness of the strand is significantly reduced, simply because the strand stiffness is the harmonic mean of the stiffness of its cross-sectional slices. When a straight strand weakens, the force it carries is redistributed to adjacent strands; as a result, the boundary conditions of the breaking strand is best described as a constant deformation. For a non-*straight* strand loaded in tension, elastic bending energy is distributed over the whole strand, not just its neck.
Consequently, bonds breaking at the neck do not significantly change the apparent tensile stiffness of the strand; non-straight strands are thus subjected to constant force boundary conditions during fracture. Therefore, we explore two scenarios for strand rupture events: constant strand force $F$, or constant strand deformation, which corresponds to a constant bond force $f$.

We begin by examining the high stress limit, when $k'_D \gg k_A$, at constant deformation of the strand. In this case, association events are rare and negligible. The probability that a single bond is still intact at time $t$ after the application of a static load is $p_1(t) = \exp(-k'_D t)$. Then, the probability that a strand with a cross-section of $n$ particles is still intact at time $t$ becomes $p_n(t) = 1 - (1 - p_1(t))^n$. We integrate to find the average strand survival time $\tau_D$, which yields the dissociation rate of the strands,

$$K_D = \frac{1}{\tau_D} = \left( - \int_0^\infty t \frac{dp_n}{dt} dt' \right)^{-1} = \frac{k'_D}{S_n} \approx \frac{k'_D}{\epsilon + \ln n}. \quad (5.2)$$

Here, $S_n = \sum_{j=1}^{n} 1/j$ and $\epsilon = 0.5772\ldots$ is Euler’s constant. The last approximation of Eq.(5.2) holds for large values of $n$. Thus, at high applied loads the dissociation rate of a strand with many bonds in its cross-section is almost the same as the dissociation rate of the individual bonds that make up the strand.

If instead a constant force $F$ is applied to the strand, the force on each bond becomes $f = F/j$. When $j$ bonds remain, the time until the subsequent bond rupture is exponentially distributed with rate parameter $jk_D \exp(F\delta/jk_B T)$. The rate at which strands break can be estimated using the sum of expected times between each bond rupture,
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\[ K_D \approx \left[ \sum_{j=1}^{n} \frac{1}{j k_D} \exp \left( -\frac{F \delta}{j k_B T} \right) \right]^{-1} \]  

(5.3)

By substituting \( x = j/n \) and assuming that \( n \) is large, we obtain

\[ K_D \approx k_D \left[ \sum_{j=1}^{n} \frac{1}{x} \exp \left( -\frac{F \delta}{n k_B T} \cdot \frac{1}{x} \cdot \frac{1}{n} \right) \right]^{-1} \]

\[ \approx k_D \left[ \int_{0}^{1} \frac{1}{x} \exp \left( -\frac{F \delta}{n k_B T} \cdot \frac{1}{x} \right) dx \right]^{-1} \]

\[ = \frac{1}{E_1(F \delta/n k_B T)} \cdot k_D \exp \left( \frac{F \delta}{n k_B T} \right) \]  

(5.4)

In the final approximation, the exponential integral \( E_1(z) = \int_{1}^{\infty} \frac{1}{t} \exp(-zt) dt \) is approximated using elementary functions for convenience \([91]\). According to Eq.\((5.4)\), the strand dissociation rate for constant strand force is much increased as compared to constant strand deformation in Eq.\((5.2)\).

In the low stress limit, when \( k'_D \ll k_A \), bond dissociation events are followed almost immediately by an association event. Consequently, all bonds of the cross-section must break within an \( \mathcal{O}(1/k_A) \) time for a strand to break, thus making strand rupture a much more rare and cooperative event. We use the following thought experiment to derive the dissociation rate of strands: Assume that the fracture gap does not widen when the strand breaks. Then, the probability that one particular bond of the cross-section is broken at a given time is \( P_1 = k'_D/k_A \). The probability that all bonds are broken is \( P_1^n \). That is, \( P_1^n \) is the fraction of time that the strand spends in the broken state. At the point of strand fracture, the expected time before
one of the bonds reform and restore the strand is $1/nk_A$. Thus, $1/nk_A$ is the typical duration of each fracture. This yields the dissociation rate of strands

$$K_D \approx nk_A P^1_i = nk_A \left( \frac{k_D}{k_A} \right)^n \cdot \exp \left( \frac{nf\delta}{k_B T} \right). \quad (5.5)$$

Now, suppose the gap is allowed to widen as a strand breaks. This precludes the re-association of bonds after the strand fracture event. However, for an intact strand, the dissociation rate cannot depend on the future fate of the strand after fracture due to the laws of causality. Hence, the strand dissociation rate must still be given by Eq.(5.5) when strand fracture is irreversible.

### 5.2.3 Macroscopic model

At the macroscale, we take a mean-field approach. When a small stress is applied to a statistically homogeneous material, the initial microscopic strand fractures are distributed over the volume of the sample [92, 93]. We assume that the degradation proceeds in this dispersed failure mode, preserving spatial homogeneity. Eventually, there is damage localization, which means that cracks much larger than the mesh size of the pristine material form. This finally leads to critical fracture and macroscopic failure of the material. We propose that the delay time is well estimated by the time-scale of the initial static fatigue, occurring prior to the final macroscopic failure, while the duration of critical crack propagation, which is much more rapid, can be neglected.

Consider a strand structure of characteristic mesh size $\xi$. The area density of strands in a hypothetical yield surface is $\rho \sim 1/\xi^2$. From a mean-field, equal load-
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sharing approximation, the tensile and transverse shear force components on a strand becomes,

\[
\langle F \rangle|_{\hat{p}} = (\sigma \cdot \hat{p}) \cdot \rho(\hat{p}) \tag{5.6a}
\]

\[
\langle F \rangle_\perp(\hat{p}) = |(\delta - \hat{p}\hat{p}) \cdot (\sigma \cdot \hat{p})|/\rho(\hat{p}), \tag{5.6b}
\]

respectively. Here, overbars are used to denote spatial average, \(\sigma\) is the stress tensor, \(\delta\) is the unit tensor and \(\hat{p}\) is the unit vector in the axial direction of the strand. The axial force \(\langle F \rangle|\) modifies the bond energy barrier as previously described. We assume that a finite shear force \(\langle F \rangle_\perp\) across the strand also leads to enhanced dissociation, lowering the energy barrier of each bond by a factor \(\alpha \langle F \rangle_\perp \delta/jk_B T\), where \(\alpha > 0\) is a constant factor. The two components \(\langle F \rangle|\) and \(\langle F \rangle_\perp\) both contribute to the effective strand force \(\langle F \rangle\) controlling the strand dissociation rate. As a first-order approximation, we make the linearization \(\langle F \rangle = \langle F \rangle| + \alpha \langle F \rangle_\perp\). The strands with highest dissociation rate are oriented in the direction which maximizes \(\langle F \rangle(\hat{p})\).

In a simple shear geometry with an applied shear stress \(\sigma_{12}\), the effective strand force can be written as \(\langle F \rangle = \sigma/\rho\), where \(\sigma \sim \sigma_{12}\). For the constant strand force assumption, we thus have \(F = \langle F \rangle = \sigma/\rho\), while for the constant strand deformation assumption, we have \(f = \langle F \rangle/n = \sigma/n\rho\).

Strands break with a dissociation rate \(K_D\) and re-form with an association rate \(K_A\). This dissociation/association dynamics leads to a birth–death type ordinary differential equation (ODE) for \(\rho = \rho(\hat{p}, t)\). We drop the direction-dependence of \(\rho\) for brevity, understanding that we study the most probable fracture plane,
\[ \frac{d\rho}{dt} = -K_D\rho + K_A(\rho_0 - \rho) , \quad \rho(0) = \rho_0, \]  
(5.7)

where \( \rho_0 \) is the initial area density of strands. Here, \( K_D \) is a function of \( \rho \) through the effective bond force \( \langle F \rangle \). As \( \rho \) diminishes, the material becomes weaker, \( \langle F \rangle \) increases and the strand dissociation accelerates.

We take the characteristic delay time \( \tau \) to be the time required for \( \rho \) to decrease from \( \rho_0 \) to \( \rho_0/e \). It is straight-forward to compute \( \tau \) by solving Eq.\( (5.7) \) numerically. The predicted behavior is, however, not directly apparent from the ODE.

For the constant strand deformation assumption and negligible association rate of strands, \( K_A = 0 \), it is possible to obtain an analytical estimate for \( \tau \). We have,

\[ \frac{d\tilde{\rho}}{d\tilde{t}} = -\tilde{\rho} \exp \left[ \tilde{n} C\sigma \left( \frac{1}{\tilde{\rho}} - 1 \right) \right] , \quad \tilde{\rho}(0) = 1, \]  
(5.8)

where \( \tilde{\rho} = \rho/\rho_0 \) is non-dimensional area density, \( \tilde{t} = tK_D|_{t=0} \) is non-dimensional time, \( C = \delta/n_0k_BT \) has the dimensions of compliance and

\[ \tilde{n} = \begin{cases} 
  n , & k'_D \ll k_A \\
  1 , & k'_D \gg k_A 
\end{cases} \]  
(5.9)

When \( \tilde{n}C\sigma \gtrsim 1 \), which according to our experiments is the case for strong gels, numerical solutions of Eq.\( (5.8) \) show that the non-dimensional delay time is \( \tilde{\tau} \approx 1/\tilde{n}C\sigma \). Returning to dimensional form, we arrive at the main result,

\[ \tau \approx \begin{cases} 
  \frac{1}{n^2k_A} \left( \frac{k_A}{k_D} \right)^n \cdot \frac{1}{C\sigma} e^{-nC\sigma} , & k'_D \ll k_A \\
  \frac{s}{k_D} \cdot \frac{1}{C\sigma} e^{-C\sigma} , & k'_D \gg k_A 
\end{cases} \]  
(5.10)
Equation (5.10) predicts two stress regimes separated by a critical stress $\sigma_c$. Solving $k_A = k_D'$ for $\sigma_c$ yields

$$\sigma_c = \frac{1}{C} \cdot \ln \frac{k_A}{k_D}. \quad (5.11)$$

By virtue of the analytical solution (5.10), it is immediately obvious that two stress regimes of different exponential scaling should be seen in the delay time. This will be discussed in experiments[3].

### 5.3 Experiments on colloidal gel failure

Rheological experiments are carried out on a stress controlled rheometer (MCR501, Anton Paar) in a concentric cylinder geometry. We study a strong gel of carbon black particles in tetradecane at 8 wt% (CB). The elastic modulus of the sample is $G_0 = 7690$ Pa and is measured before each experiment to confirm that the sample has not evolved due to evaporation or particle migration. To establish reproducible initial conditions they are presheared for 60s at a shear rate of $\dot{\gamma} = 500$ s$^{-1}$ and left to recover for 15 minutes before starting the measurement.

For very low $\sigma$, the initial creep response is purely elastic: the strain initially increases linearly with time, followed by an inertial ringing reflecting the elasticity of the sample[94] after which the strain becomes nearly independent of time. Virtually no creep is observed over the full length of the experiment, dashed line in Fig.5.2. However, as $\sigma$ is increased the initial response remains the same, but the time-independent creep persists only for a finite time, whereupon the sample fails catastrophically and the strain increases sharply as shown in Fig.5.2a. This occurs after a delay $\tau_{d}$, which we take to be the point of maximum shear rate. As $\sigma$ is
increased $\tau_d$ decreases (Fig. 5.2a). Ultimately, the range over which the creep is time-independent becomes very small and failure is nearly instantaneous. After failure, the modulus is essentially unchanged but the gel yields at significantly shorter times, unless it is rejuvenated by a strong pre-shear treatment.

### 5.3.1 Delay time

Similar behavior is observed for polymer gels, where it is understood quantitatively as the result of an activated process with an energy barrier originating from the breaking of physical bonds that provide the crosslinks in the network. Based on this simple assumption from polymer gels, we might expect a single exponential decay of $\tau_d$ with applied $\sigma$. To test if this simple microscopic prediction holds for colloidal gels, we plot $\tau_d$ as a function of $\sigma$ on a semi-logarithmic plot. Surprisingly, rather
than the single exponential decay, we instead observe two distinct exponential regimes (triangles in Fig. 5.3). To account for the more complex behavior observed for colloidal gels, we generalize the bond-rupture model, Sec. 5.2.2. Within this model $\tau_d$ is approximated by the time required for the rupture of a single bond due to thermal fluctuations. The rate of this rupture is increased by the applied stress. However, this picture is based on the behavior of a single bond; it ignores the actual structure of a colloidal gel. In contrast to the structure of a polymeric gel, colloidal gels are highly heterogeneous: particles aggregate into a network of mesoscopic strands which form a mechanically stable, percolating network. These strands can be many particles wide; therefore they do not break directly when only a single bond ruptures. Instead their integrity is maintained by the adjacent bonds and thermal fluctuations can lead to reformation of a broken bond. Catastrophic failure of a strand occurs only when all bonds across the strand break simultaneously.

At sufficiently high $\sigma$, interparticle bonds rupture at a higher rate than they reform; then the breaking of entire strands occurs at approximately the same rate as the breaking of single bonds. We expect that catastrophic failure of the network occurs very rapidly; this reduces to the behavior predicted by the single-bond rupture model leading to the exponential dependence observed at high $\sigma$. By contrast, in the limit of low $\sigma$, the bond-breaking rate is smaller than the bond-reforming rate; thus the rupture of a strand is much more unlikely and occurs only in the rare event of simultaneous dissociation of all bonds in its cross-section. This also leads to an exponential dependence of $\tau_d$ on $\sigma$ but with a different characteristic stress. This accounts for the two distinct regimes of delayed yield observed experimentally (triangles in Fig. 5.3):
Figure 5.3: Delay time $\tau_d$ between the application of the shear stress $\sigma$ and the moment of yield, for gels of strong gel of carbon black at 8 wt% (triangles), depletion gel of polystyrene colloids and dextran ($\phi = 0.3$, $c_p = 50$ mg/ml, circles) and thermoreversible gel of pNIPAm-grafted colloids at $\phi = 0.075$ (squares). Drawn lines are exponential fits, according to Eq. 5.10. Inset show magnifications of the data for weak depletion and thermoreversible gels.
a rapid, catastrophic rupture of the structure at high stresses and a slow, stochastic erosion of the structure at low stresses, see Sec. 5.2.2.

5.3.2 General behavior of colloidal gels

This behavior should be intrinsic to all gels. To explore the generality of our description we investigate a very weak gel formed by polystyrene particles (d = 480 nm, φ = 0.35)(PS) suspended in a mixture of $H_2O/D_2O$, for buoyancy matching, and with a depletion attraction induced through the addition of 50 mg/ml dextran of $\sim 200$kg/mol. This gel is much weaker with $G_0=203$ Pa. The delayed yielding response is similar in form to Fig. 5.2(b). Moreover, $\tau_d$ again exhibits two distinct exponential regimes, circles in Fig.5.3. We also study a gel formed with polystyrene colloids (d=430 nm) onto which the thermoresponsive polymer pNIPAm is grafted. These are suspended in a mixture of $H_2O/D_2O$ at $\phi = 0.075$. They can be made adhesive by increasing the temperature above the lower critical solution temperature of the polymer, causing them to gel[95]. For $\phi = 0.075$ the gel exhibits $G_0=2689$ Pa and displays two clear exponential regimes, squares in Fig.5.3. These results confirm the universal nature of the delayed yielding response of colloidal gels.

5.3.3 Effects of preshear on gel strand structure

One method of making gels more resilient to delayed yielding is to increase the ratio between association and dissociation rates, $k_A/k_D$, of individual bonds, which promotes the stability at low stresses, as predicted by Eq.(5.10). This would require changes in the chemistry of the system. For products such as cosmetics or food,
changing chemistry often has adverse effects on other critical product properties. However, this multiscale model also predicts a significant effect of the mesoscale structure on the delayed yielding time. This structure can be modified for instance by changing volume fraction[82], applying a preshear[83, 96] or by changing the quench history, for instance by allowing the strands to coarsen at a shallow quench before making the gel thermally stable at a deeper quench[82].

A colloidal gel is formed in a suspension of index and density matched particles, made attractive by addition of a linear polymer which induces a depletion attraction between the particles, see Chapter 3. After formation, a confocal microscopy image shows that the gel has a finely stranded structure as shown in Fig. 5.4a, characteristic of irreversible gelation. Upon applying a constant shear rate, $\dot{\gamma} = 0.01 \text{s}^{-1}$, we see the gel evolving in time in the sequence of images as seen in Fig. 5.4; the initially finely-stranded gel becomes gradually more coarse and heterogeneous, due to disproportionation of the gel structure. When the applied preshear exceeds a total strain of approximately $\gamma_{pre} = 1$, anisotropy develops in the structure. The coarsening of the structure leads to decreasing strand area density $\rho_0$ and thus an increase of the compliance parameter $C$ with preshear. The coarsening of the structure should also increases $n$.

A critical component of our explanation is the structure and, specifically, thickness of individual strands, $n$. While difficult to experimentally measure for the refractive index matched gel sample in Fig. 5.4, we can explore these effects we modify the strand structure while maintaining both the attraction energy and $\phi$ constant. To accomplish this we use thermoreversible gels made from stearylated-silica particles
Figure 5.4: Confocal microscope images of an index and density matched colloidal gel for different amounts of preshear $\gamma_{pre} = 0, 1, 2, 3$. The shear-gradient plane is imaged with upward flow direction. The volume fraction is $\phi = 0.15$.

(2$r = 160$ nm) (SiO2) suspended in dodecane. These systems undergo a fluid-gel transition when cooled below 29°C [5], but can be rejuvenated prior to each new measurement by heating to 40°C. A fine-stranded structure is formed by rapidly cooling the sample to 5°C; for $\phi = 0.25$ the as-formed gel has $G_0 = 6233$ Pa and exhibits a single exponential regime as seen as circles in Fig.5.5 indicative of $n=1$. After gelation, the structure can be coarsened by applying a mild preshear as seen in Fig.5.4[60]. Application of a linear pre-strain pre results in a gel whose linear viscoelastic properties are unchanged. However, the gel becomes dramatically less resilient to yielding; for a given $\sigma$, $\tau_d$ decreases by many orders of magnitude. For weak colloidal gels, application of a pre-strain induces a thickening of the strands[60]. Interestingly, upon application of a prestrain to thermoreversible silica gels the initial single exponential regime transforms into two distinct regimes in $\tau_d$ (Fig.5.5). The ratio of the slopes of the two exponential regimes increases from $n=1$ at $\gamma_{pre} = 0$ to $n=6$ for $\gamma_{pre} = 3$; this reflects the increasing thickness of the strands. These data
Figure 5.5: $\tau_d$ versus $\sigma$ for thermoreversible gels of C18-grafted silica (SiO2) after the application of various $\gamma_{pre}$. Inset shows the distribution of breaking times at $\phi=0.25$ and $\sigma=8$ Pa, drawn line is the predicted log-normal distribution.

highlight the pivotal role of mesoscopic structures.

5.3.4 Comparing model to experiments

The four unknown parameters of the proposed model, $k_D$, $k_A$, $n$ and $C$ can be obtained directly from the slopes and intercepts of the two regimes[3]. Alternatively, they can be obtained from a fitting procedure using numerical solutions of Eq.5.7. The extracted parameters are compiled in Table 5.1, in which the data is sorted in ascending order of gel strength.

Interestingly, both structural and dynamic parameters that characterize the gels can be obtained from a single type of rheology experiment. As the depth of the interaction potential increases, going from weak to stronger gels in Table 5.1, the typical elastic energy $W = \sigma c C$ required to initiate erosion increases. Here, $W$ is
Table 5.1: Structural parameters for various gel systems obtained from delayed yielding experiments and Eq. (5.7): strand coarseness $n$, bond ‘compliance’ $C$ and quiescent bond dissociation and association rates $k_D$ and $k_A$. Here, $\sigma_c$ is the computed critical stress separating the stress regimes and $W$ is the typical elastic energy at break, normalized by $k_B T$.

<table>
<thead>
<tr>
<th></th>
<th>$\phi$</th>
<th>$\gamma_{pre}$</th>
<th>$n$</th>
<th>$C$</th>
<th>$k_D$</th>
<th>$k_A$</th>
<th>$\sigma_c$</th>
<th>$W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>30</td>
<td>3000</td>
<td>17</td>
<td>1.5</td>
<td>4.5⋅10$^{-2}$</td>
<td>0.08</td>
<td>0.38</td>
<td>0.2</td>
</tr>
<tr>
<td>CB</td>
<td>8 wt</td>
<td>3000</td>
<td>25</td>
<td>0.045</td>
<td>2.6⋅10$^{-1}$</td>
<td>0.75</td>
<td>24</td>
<td>0.7</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>25</td>
<td>0</td>
<td>1</td>
<td>0.33</td>
<td>7.0⋅10$^{-3}$</td>
<td>0.60</td>
<td>13.5</td>
<td>4.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>25</td>
<td>3</td>
<td>3</td>
<td>0.90</td>
<td>7.0⋅10$^{-3}$</td>
<td>0.60</td>
<td>4.9</td>
<td>4.5</td>
</tr>
</tbody>
</table>

normalized by $k_B T$.

5.4 Chapter summary

The delayed yielding of colloidal gels is strongly affected by their hierarchical structure. In the limit of small stresses, failure of individual strands is stochastic; several bond dissociation events must occur almost simultaneously for a strand to break. A quantitative prediction of the delay time is derived from the association/dissociation dynamics of colloid bonds, the strand coarseness and mesh size. After quenching, the gel structure is arrested spinodal and finely stranded. In this case, the delayed yielding time decreases exponentially with increasing stress. In the low stress limit, it is predicted in Eq. 5.10 that coarse-stranded gels are stronger from the point of delayed yielding. If a gel is allowed to coarsen by maintaining it at a shallow quench for some time, and then is stabilized by a deeper quench, this coarser structure will
perform better in delayed yielding, which is also observed experimentally.

When a preshear is applied to the gel, slack is pulled out of its structures so that strands become straighter. At sufficient amounts of preshear $\gamma \gtrsim 1$, two distinct stress regimes appear, where delay time increases exponentially with decreasing stress, but with different exponential factors in the two regimes. Some of the gel strands break during preshear and the dissociation rate is further enhanced as the force on the remaining strands increases. Consequently, preshear reduces the delay time.

Although the delayed yielding in simple shear is not directly shown to govern gravity-induced delayed collapse, we emphasize this possibility, particularly for strong gels, which are otherwise thermally stable under quiescent conditions. It is clear from the explicit relation between the general stress tensor and the strand dissociation rate, that the proposed erosion mechanism is present in both shear and compression. Indeed, gravity induces both compressive stresses in the bulk of the gel and shear stresses near adhesive vertical walls of its container [78, 77], either of which could cause delayed collapse.

Delayed yielding and the difficulties in its prediction is a problem for a wide range of heterogeneous solids, including steel [97], wood [98], ceramics [99] and soft solids [4, 79]. Although delayed yielding in these materials have somewhat different physical origin on the microscopic level, it originates from the interplay between thermal fluctuations, structure, applied stresses and sometimes corrosion phenomena. Colloidal gels, by virtue of their clear separation of structural length-scales, can be regarded as simple model systems for studying these common yielding mechanisms of heterogeneous solids.
Publication from this work:

5.5 Experimental for this chapter

5.5.1 Rheology

Rheological experiments are carried out on a stress controlled rheometer (MCR501, Anton Paar) in a concentric cylinder geometry. We study a strong gel of carbon black particles in tetradecane at 8 wt%. The elastic modulus of the sample is $G_0 = 7690$ Pa and is measured before each experiment to confirm that the sample has not evolved due to evaporation or particle migration. To establish reproducible initial conditions they are presheared for 60 s at a shear rate of $\dot{\gamma} = 500$ s$^{-1}$ and left to recover for 15 minutes before starting each creep measurement.

5.5.2 Rheoconfocal

Direct imaging of gel structure with $\gamma_{pre} > 0$ is achieved by combining a spinning-disk confocal (Yokogawa CSU22) with a commercial rheometer (Malvern, HR Nano). A custom Couette geometry allows for the observation of the shear-gradient plane across the entire gap. Gels are subjected to a strong preshear $\dot{\gamma} = 200$ s$^{-1}$ for 60 s with an equilibration time of 5 min, or until the gel visually does not undergo structural
rearrangement in the observed field of view, $\sim 100 \mu$m. The sample is then strained continuously at a shear rate of $\dot{\gamma} = 0.01 \text{s}^{-1}$; images are captured throughout up to $\gamma_{\text{pre}} = 3$. 
Chapter 6

Inducible colloidal attraction - AFM and syneresis

As highlighted in Chapter 5, colloidal gels are extremely history dependent: Their mechanical and thermodynamic history often dominates their rheological response. It is therefore not just ideal, but necessary to induce attractions in situ whether it be inside a rheometer or another container as seen in this chapter. As most experimental investigations on colloidal gels overlook this step and strictly focus on what occurs after, certain phenomena are simply not observed specifically syneresis. Syneresis is the isotropic compaction and concomitant expulsion of fluid from a gel is rarely observed in laboratory colloidal systems. However, it is nearly ubiquitous in food products such as cheese and yogurt; this disparity is not fully understood. This chapter is broken into two parts: synthesis and characterization on the molecular, colloidal, and bulk scale of a temperature sensitive surfactant which permits the second part; colloidal syneresis of model systems that addresses the aforementioned
6.1 Thermosensitive molecular, colloidal, and bulk interactions using a simple surfactant

Assembly of colloidal or nano-particles into ordered, or disordered, packings can be achieved in a variety of ways. Some of these require external energy input, such as methods involving capillary shaping of crystals at the drying front of a fluid meniscus [100] or methods that use external fields to drive ordering, such as electric fields [101] or shear and compressional flow [58]. Alternatively, the formation of nano- and microstructured materials may be achieved by tuning or triggering the attractive and/or repulsive interactions between the nanoparticles in absence of any external driving forces, an approach known as self-assembly. Tunable forces between the surfaces of the nanoparticles, greatly enhances the fidelity of the self-assembly process. In recent years, inspiration has been taken from nature, using complementary DNA strands to trigger the attraction-driven self-assembly of DNA-coated particles. While successful and versatile, such a bio-inspired approach suffers from significant drawbacks. The high binding affinity of the complementary DNA strands inhibits crystallization due to trapping of the system in a kinetically arrested state; as a result crystal formation only occurs in a very small window of environmental parameters [102]. Moreover, protocols for grafting biomolecules to the surface of nanoparticles typically involve several chemical modification steps [103]. This example illustrates a need for straightforward and inexpensive methods with which the interactions between arbitrary colloidal par-
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ticles can be made precisely responsive to environmental triggers.

The availability of such methods would not only have important applications in the fields of nanostructured colloidal materials but also in industrial applications. Many consumer products, such as coatings [104], foods [105], and cosmetics, use networks of weakly aggregated particles, known as colloidal gels, to impart a soft-solid mechanical behavior to these otherwise fluid products. If the attraction forces between the particles, ultimately responsible for the network formation of the particles, were tunable, it would greatly improve not only processability but also the control of the material properties [4]. In the same fashion, environmentally-triggerable attractive forces between microscopic particles could be used to trigger on-demand phase inversion of emulsions [106], which may greatly facilitate emulsion-based separation processes, film formation in drying emulsion paints and the recovery of crude oil from waterflooding-based enhanced oil recovery [107].

In this section, we demonstrate a novel and facile method for rendering the interactions between almost any type of colloid, ranging from polymeric latex particles to emulsion droplets, thermoresponsive. This is accomplished by the one-pot synthesis of a thermoresponsive surfactant, through chain-transfer polymerization of poly(N-isopropyl acrylamide), which is subsequently spontaneously adsorbed to the surface of the colloid. The spontaneously assembled thermoresponsive brush instantaneously imparts a temperature-tunable attractive potential between particles. We directly quantify these interactions using Colloidal Probe Atomic Force Microscopy. To demonstrate the versatility of our method, we show that it reversibly triggers gelation and crystallization in colloidal dispersions and induces phase inversion on-
demand in an otherwise stable oil-in-water emulsion.

We use the well-known lower critical solution temperature (LCST) behavior of poly N-isopropylacrylamide (pNIPAm) to induce a thermoresponsive attraction between colloidal particles [108]. While strategies for grafting pNIPAm polymers from the surfaces of colloidal particles have been described [109], these involve rather complicated chemical protocols in the presence of the particles, such as surface-initiated free-radical or atom transfer radical polymerizations. Here we take a more simple and versatile approach; we synthesize a surfactant based on pNIPAm. The addition of the chain transfer agent, 1-octadecanethiol, to a free radical polymerization of pNIPAm, results in C18-alkyl end-capped pNIPAm chains; thus forming a thermoresponsive surfactant in a single step. This reaction is performed on a large scale, in this study we prepare ~100g of the surfactant with an estimated yield of approximately 92%. GPC analysis reveals a molecular weight $M_n = 5.2$ kg/mol, corresponding to approximately ~45 NIPAm monomers per surfactant with a polydispersity $M_w/M_n = 2$; this broad size distribution results from free radical polymerization and might in future work be improved through more controlled polymerization methods [110].

### 6.1.1 Direct measurement of surface forces

In Colloid Probe Atomic Force Microscopy (CP-AFM) (Fig.6.1a), a large probe particle is glued to an AFM cantilever; bringing this colloidal probe in contact with a flat surface of identical chemistry allows the direct measurement of the force $F$ between the surfaces as a function of their separation distance $h - h_0$ [111]. After adsorbing the thermosensitive surfactant onto both the hydrophobic colloid and
substrate, an attractive potential develops as the surfactant-coated system is heated above its LCST (6.1b), which we find to be 32°C. Above the transition temperature an interface forms between the polymer-rich nanoscopic pNIPAm layer and the bulk solution; this interface is characterized by a low interfacial tension, calculated using JKR theory \cite{112} to be \( \sim 10 \text{mN/m} \) at 35°C, as measured using a Surface Force Apparatus \cite{113}. Upon contacting two opposing layers of this collapsed polymer, an adhesive interaction results between the two surfaces. Interestingly, this adhesive interaction continues to increase in strength as we increase the temperature above the LCST, from a total adhesion force of 0.2nN at 32°C to 3.4nN at 44°C. This suggests that the interfacial tension between collapsed pNIPAm and its surroundings are dependent on temperature (Fig.6.2a). We conclude that this is a direct consequence of the water content of collapsed pNIPAm above its LCST; this has been measured by
various methods at 40°C [114]. However, these values appears to be very sensitive to the exact molecular weight and grafting density of the polymer [113, 115].

Additionally, we observe a clear dependence of the adhesion magnitude on the retraction velocity, \( v_r \). We define the peak pull-off force, \( F_p \), as the magnitude of the attractive minimum for each retraction curve; \( F_p \) clearly increases with an increase in \( v_r \) (Fig. 6.2b). This is consistent with the separation of two polymeric brushes that have formed entanglements or other adhesive contacts [54]. This time-dependence on the adhesive forces obscures the true equilibrium interaction forces experienced by colloidal particles that are only thermally excited. To access the equilibrium adhesion, we extrapolate the peak pull-off force to \( v_r = 0 \). The interfacial or adhesion energy per unit area is estimated using the Dejaguin approximation using the exact size of our colloid probe (2\( r \approx 8.6 \mu m \)), the extrapolated \( F_p(v_r = 0) \) and the interaction range, \( L \). We estimate this interaction range by fitting the repulsive rise, at separations smaller than the attractive minimum, to a linear fit defining the constant compliance regime (solid line in Fig. 6.2a), from which we approximate the true surface separation at \( F_p \) from the constant compliance line. We find that the \( \langle L \rangle \sim 8nm \) for all investigated conditions as this length is predominately set by the \( R_g \) of absorbed surfactant. The resulting interfacial energy shows a nearly linear dependence on temperature above the LCST (Fig. 6.2c); this illustrates that within our simple approach the attractive force between colloidal or nanoparticles is accurately tuned using temperature as a dial.

So far, we showed results in which the contact time between the colloid probe and surface is held constant at 10sec. However, we may also vary the time that
Chapter 6: Inducible colloidal attraction - AFM and syneresis

Figure 6.2: Force-separation curves at various temperatures in 0.05gL\(^{-1}\) pNIPAm surfactant in 100mM NaCl. (a) retraction curves from bottom to top at \(T = 44, 40, 38, 36, 34, 32\) and 28\(^\circ\)C with a constant contact time (10sec) and velocity \(v_r = 100\text{nm/s}\); solid line is a linear fit to determine the constant compliance regime for each retraction curve (b) averaged peak force, \(F_p\), for at least 15 individual retraction curves at several velocities using large separation, \(h - h_0\), values to normalize retraction curves. (c) True adhesion energy using the Dejaguin approximation and the extrapolated \(F_p\) for \(v_r = 0\); line is a linear fit to temperatures above the LCST (d) Average peak force, \(F_p\), versus contact time below (28\(^\circ\)C, •) and above (36\(^\circ\)C, ■ and 45\(^\circ\)C, ▼) the LCST of the surfactant; lines are logarithmic fits.
both surfaces are in contact by applying a surface delay between the approach and retraction curves; we aim to keep the surface in contact at a more-or-less constant load force of 10nN. As we vary the contact time, we find a logarithmic increase in $F_p$ with contact time for temperatures above the LCST; this is reminiscent of aging of glassy contacts in other surface phenomena (Fig. 6.2d) [116]. This aging of the adhesive contact, resulting in increasing peak force is most likely a result of polymer chain interpenetrate over time, which is a self-quenching process due to interpolymer friction [54, 117]. Note that it could also be the result of hindered diffusion of water from the narrow collapsed polymer film between the two surfaces. The latter effect should saturate at long contact times which we do not observe and unfortunately longer surface delays become experimentally infeasible due to thermal drift of the cantilever. As a result, while the magnitude of the attraction between surfaces is tunable with temperature, the attraction is time-dependent. This feature, as we will show below, aids in the high-fidelity assembly of crystals and finally freezing in of the assembled structures over time.

### 6.1.2 Bulk assembly

Colloidal particles onto which the pNIPAm-based surfactant is absorbed display temperature tunable self-assembly that is fully reversible. We adsorb the surfactant onto the surface by temperature cycling a suspension of particles above and below the LCST in the presence of the surfactant. In this manner, nearly any colloidal dispersion can be modified without complicated grafting methods [109]. Due to the equilibrium nature of surfactant adsorption some micelles are present in the bulk
solution and in all experiments a small excess of surfactant is present; 50mg/L is the concentration in solution. We use monodispersed sulfate stabilized polystyrene colloids synthesized through surfactant-free polymerization ($2r = 0.436\mu m$). At temperatures below the LCST, the surfactant layer present on the particle surface acts to stabilize the dispersion, however upon heating to the LCST, the system undergoes reversible aggregation.

It should be emphasized that controlling the adhesion of individual colloidal particles onto the surface of the dispersion’s container, such as coverslips or rheological geometries, is crucial. If the surface is unmodified, individual colloidal particles absorb to the fixed boundary above the LCST preventing rearrangement and hindering efficient assembly. We prevent surfactant absorption at temperatures above the LCST to the container surface through the use of polyelectrolyte multilayers (PEMs) [118]. For rheologic measurements, we do not modify any surfaces and thus upon heating the dispersion forms an arrested network of nanoparticles called a gel (Fig.6.3a,b) [119].

We monitor the onset of elasticity in a concentrated suspension of pNIPAm-modified polystyrene particles upon heating the dispersion. This elastic response is measured using rheology by applying a small constant oscillatory strain ($\gamma = 0.2\%$) to the colloidal particle dispersion and calculating the in-phase storage (elastic, $G'$) and out of phase loss (viscous, $G''$) moduli [119]. As the dispersion is heated above LCST of the surfactant, we find that the elastic modulus $G'$ shows an immediate increase of several orders of magnitude followed by a slow approach to a plateau. Unlike other particle gel systems, $G'$ and $G''$ are of the same order of magnitude,
Figure 6.3: Temperature tunable bulk response of a colloidal dispersion, $2r = 436\,nm$ with adsorbed surfactant in 0.05gL$^{-1}$ pNIPAm surfactant in 100mM NaCl. (a) confocal reflectance microscopy of the colloidal dispersion $T = 28^\circ C$ and (b) above the LCST of the surfactant $T = 40^\circ C$ at $\phi \sim 5\%$, scale bar = 15$\mu m$. (c) (●) Elastic modulus, $G'$, as measured with oscillatory rheology of the particle dispersion at $\phi = 0.10$ after 5hrs at temperatures between 32$^\circ C$ and 42$^\circ C$ (■), interfacial energy measured by AFM as in Fig.2c; dashed lines are linear fits (d) $G'$ during 5 temperature cycles between 15$^\circ C$ and 45$^\circ C$ (e) temperature profile during cycling
highlighting the highly flexible or dissipative interaction between individual colloidal particles. The magnitude of this plateau increases linearly with the distance to the LCST, $T - T_{\text{LCST}}$. Remarkably, the magnitude of the elastic plateau of a bulk particle dispersion follows exactly the same linear dependence found in the colloidal probe AFM measurements (Fig.6.3c); this suggests a one-on-one relation between the forces measured with AFM to the macroscopic rheology. The elastic moduli of colloidal gels are typically governed by the stretching, not bending, of the interparticle bonds; $G' \sim \kappa(\xi)/\xi$, with that $\kappa(\xi) \sim \kappa_0/N_{\text{chain}}$ where $\kappa_0$ is the individual bond spring constant, $N_{\text{chain}}$ is the number of colloids in a stress bearing chain, and $\xi$ is the mesh size of the network which depends on the fractal dimension, $d_f$ such that $\xi \sim 2r\phi^{-\frac{4}{3-d_f}}[120, 121]$. From these scaling arguments, we deduce that the magnitude of $G'$ is dominated by the individual spring constant, $\kappa_0$, of the bond. In turn, the spring constant is taken to be the derivative of the force-extension curve of the bond, which is exactly what we measure in our AFM experiments [122]. Assuming there is little to no change in $d_f$ and the measured interaction range is constant, $\langle L \rangle \sim 8nm$, the resulting spring constant should be directly proportional to $F_p$. This is exactly what we see in our experiments from the excellent agreement between bulk rheology and individual force-extension curves.

Strikingly, the temperature-induced assembly, or aggregation, of these colloidal particles is fully reversible. We show the rheologic results of a temperature cycling experiment where a neutrally buoyant colloid dispersion is repeatedly heated and cooled between two temperatures above and below the LCST in Fig.6.3d,e. Heating and cooling rates are low, 0.5°C/min, to minimize effects from convection. Addition-
ally, the entirety of the measurement is performed in a oscillatory fashion with no
preshear between cycles; we allow only diffusion to break up the elastic network. The
network shows minor hysteresis as a background $G'$ begins to rise after 5 cycles at
temperatures below the LCST, although the magnitude of this background is still
quite low, $G' \sim 1\text{Pa}$.

6.1.3 Colloid-scale dynamics

At the individual colloid level above the LCST, the attractive potential causes not
only the particles to assemble but also allows rapid rearrangement and crystallization.
We follow this process using larger fluorescently-labeled particles ($2r = 1.4\mu m$, $\phi \sim
5\%$) with a confocal microscope. We modify the surface of a 2-dimensional chamber
with a coating of a PEM, which eliminates adhesion of the colloidal particles to the
walls of the sample chamber.

Upon heating a dispersion of colloidal particles confined in these chambers to above
the LCST of the surfactant, isolated chains of small numbers of colloids ($N \leq 7$)
form which further assemble into larger crystallites (Fig.6.4a,b). The spatial con-
figuration of these small assemblies is highly transient, suggesting highly “slippery”
adhesive bonds. To illustrate this we measure the bond angle $\theta(t)$ between neigh-
broring particles using standard particle tracking algorithms [123]. Initially, the bond
angles fluctuated rapidly, with the average angle $\langle \theta \rangle \sim \pi$ and the average number
of bonds, $n_b \sim 2$, indicative of linear and ”slippery” configurations. Over time, $\theta$
evolves until mechanically stable and energetically favorable equilateral triangle con-
figurations, characteristic of hexagonal packings, form with $\theta \sim 1.05(60^\circ)$ and $n_b=3$
(Fig. 6.4c). This process repeats until small hexagonal crystallite regions grow, limited only by the depletion of free particles and smaller assemblies in their surrounding area (Fig. 6.4b). Interestingly, within these 2D crystallite regions colloids are still highly mobile; fluctuations in individual particle fluorescence intensity as each colloid moves in and out of the confocal volume occur throughout (Fig. 6.4b). While individual bonds are clearly very attractive \((U \gg kT)\), the entire crystallite undulates due to thermal Brownian fluctuations. This combination of highly flexible yet persistent bonds formed between collapsed pNIPAm layers readily promotes the self-assembly of highly ordered structures. However, fluctuations in \(\theta\) decrease with time above the LCST (Fig. 6.4d,e), which may be due to an increase in bond strength with time, confirmed by the logarithmic increase in adhesion energy with contact time found in the AFM measurements (Fig. 6.2d).

### 6.1.4 Triggered emulsion coalescence

Finally, we will illustrate that the same surfactant can be used to destabilize a suspension of droplets, thus triggering phase inversion on-demand. Phase inversion is relevant to many recovery and extraction processes [107] while the actual mechanism of emulsion inversion is an area of active fundamental research [124]; enabling this process to occur on demand could enhance or prove a simple experiment method to investigate inversion. An emulsion stabilized by the thermoresponsive pNIPAm-based surfactant is very stable and concentrated gravitationally to a high droplet packing fraction without macroscopic or microscopic signs of droplet coalescence (Fig. 6.5a). However, upon heating above the LCST of the surfactant, the droplets become adhe-
Figure 6.4: 2D confocal images of fluorescently labeled polystyrene colloids ($2r = 1.4\mu m, \phi \sim 5\%$) above the LCST, 40°C. (a) time series of an isolated aggregated particle strand, $N = 5$; time between images is 5sec (b) time series of a crystallite region; time between images is 5sec. (c,d,e) neighboring bond angle, $\theta$, for single chains with time for different incubation periods at 40°C: 5, 20, 60min respectively; $\theta$ defined in final frame of (a)
Figure 6.5: 2D slice using confocal microscopy of a decane emulsion ($\phi \sim 65\%$) stabilized by the pNIPAm surfactant at (a) 22°C, (b) 45°C and then cooled back to (c) 22°C (scale bar = 50$\mu$m)

vive and allows for rapid coalescence. Macroscopic phase separation ensues, leaving behind a aggregated network of collapsed surfactant (Fig.6.5b). Upon cooling, some of the emulsion spontaneously inverts (Fig.6.5c) permitting the oil to be recovered without chemical or mechanical breaking of individual droplets.

6.1.5 Section summary

In this section, we have shown a new, and simple, method for inducing thermosensitive interactions to most hydrophobic colloidal suspension. The adsorption of a thermoresponsive surfactant, generates a temperature-tunable layer on the surface of the nanoparticle. Upon heating these particles above the LCST of the surfactant, the stabilizing polymer layer collapses and becomes adhesive. The magnitude of the adhesion energy, measured with colloid probe AFM, increases linearly with temperature and logarithmically with contact time. While such a logarithmic increase in interaction energy does prohibit rearrangement on longer time scales, the time necessary for small crystallites, of order 100 particles, to assemble is short $\leq 10$ min. The
time scale for rearrangement is driven by Brownian motion and as our particles are relatively large \( (2r = 1.4\mu m) \) compared to other assembly approaches \([117]\); we would expect smaller particles \( (2r \ll 1.0\mu m) \) to assemble more efficiently. The logarithmic attraction with contact time could paradoxically serve to lock in the self-assembled structure, resisting mechanical vibration or fluid flow. This simple, yet universal, approach presented here could lead to significant benefits in achieving high fidelity self-assembly of nanoparticle building blocks which so far has been difficult to control.

Publication from this work:


### 6.2 Syneresis of colloidal gels

When colloidal particles in a dispersion are made attractive, they aggregate into fractal clusters which grow to form a space-spanning network, or gel, even at low volume fractions \( \phi \). Once a colloidal gel forms, the heterogeneous structure bonded through weak physical interactions, is immediately subject to body forces, such as gravity \([1]\), surface forces, such as adhesion to a container walls \([2]\) and shear forces as discussed in Chapter 5 \([3]\); the interplay of these forces acting on the gel determines its stability.

Even in the absence of external stresses, colloidal gels undergo internal rearrangements within the network that may cause the network structure to evolve gradually, in processes known as aging or coarsening \([4, 5]\) or fail catastrophically, in a mechan-
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Figure 6.6: Image sequence of syneresis of a gel at $\phi_0 = 0.10$ in a spherical geometry.

ical instability known as syneresis\cite{2}. During syneresis, the solid part of the network contracts, expelling the dispersed fluid. Syneresis is thought to occur due to inherent internal stresses within the gel network, which forms through arrested phase separation from the suspending fluid. A prototypic example is the syneresis of cheese curds, a colloidal gel network of caseine micelles and fat droplets, from whey, during cheese manufacturing. While mechanical failure of colloidal gels subjected to external shear or gravitational, has been studied in detail, catastrophic failure of gels due to internal stresses that accumulate during its formation, remains largely unexplored. As a result, predicting the stability of colloidal gels remains prohibitively difficult.

In this section, we investigate the kinetic densification of colloidal gels composed of particles with mechanically different contacts, but crucially, a contrast energetic attraction. The densification process follows a Darcy flow based poroelastic model where the permeability of the gel network hydrodynamically hinders the syneresis; by contrast to previous work where the kinetics of syneresis display a clear dependence on the dispersed phase viscosity due to coalescence between attractive droplets driving the homothetic sintering\cite{126}. Crucially, we do not observe coalescence; after syneresis, the gel may relax back to a fluid dispersion of droplets or particles. We define
the magnitude of syneresis as $\Delta \phi / \phi_0$, with $\phi_0$ being the initial $\phi$; the nature of the interparticle mechanical contact, not the energetic attraction, defines the magnitude of syneresis. Soft particles, emulsion droplets and rubber particles, displaying larger densification as compared to rigid particles composed of polystyrene. Furthermore, interparticle ‘sliding’, thermal angular fluctuations between neighboring particles as seen in 6.4, play a key role in syneresis which is ultimately hindered by the gel network kinetically arresting.
6.2.1 Syneresis in colloidal gels composed of polystyrene particles

A dispersion of polystyrene particles, $2r = 355\text{nm}$, in a density matched solution of 100mM NaCl, 55/45vol% $D_2O/H_2O$, with 0.1wt% pNIPAm-surfactant, is heated to 45°C in a 10ml round bottom flask. Due to the adsorbed temperature sensitive surfactant, upon heating an elastic gel network forms and the network contracts or syneresis, as seen in Fig. 6.6. Crucially, the container walls are treated with a polyelectrolyte multilayer, PEM; this surface coating prevent the colloidal particles from adhering to the surface of the container. In the presence of an adhesive boundary condition, the gel forms but kinetically arrests as the endogenous tension generated by the gel network is balanced by the more rigid container walls. It should be emphasized that nearly all experimental studies on the mechanical failure in colloidal gels do not control the adhesion, with only one previous observation hinting at syneresis in a gel composed of polystyrene spheres and only after the vial is rotated, breaking adhesive bond to the walls[127]. It should also be noted that these gels form inside the container as the attractive potential between particles is induced by heating the dispersion; no shear forces are imposed on the network by mixing or pipetting.

We calculate the change in volume fraction from the measured area change in the gel in image sequences, assuming the gel is rotationally symmetric. The gel contracts elastically reaching a plateau value in several hours, as seen in Fig. 6.8. This process of syneresis is reminiscent of a porous elastic network contracting, similar to a sponge, where the time scale for contraction is dominated by fluid drainage from the material. Such a poroelastic process well describes gravitationally driven collapse in colloidal
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gels[1]. We adopt this kinetic framework and fit the syneresis process using,

\[ \frac{\phi(t) - \phi_0}{\Delta \phi} = (1 - e^{-t/\tau}) \] (6.1)

where \( \tau \) is the characteristic time scale for gel relaxation; this time scale is dominated by \( \phi_0 \) which sets the initial permeability, \( k_0 \), of the network such that

\[ \tau \sim \frac{\eta(1-\phi_0)R^2}{k_0K} \]

where \( \eta \) is the viscosity of dispersed aqueous phase, \( R \) is the container radius, and \( K \) is the bulk modulus of the gel. Here we use the bulk modulus not the shear modulus of the gel as it is isotropically contacting. The permeability of a gel scales inversely with fractal dimension of the network, \( d_f \), such that

\[ k_0 = \frac{a^2 \phi^2}{\phi^{2/3}} \] [1].

For \( \phi_0 = 0.10 \), we measure \( \tau \sim 500 \)s as seen in the Fig.6.7 inset; from this value, we calculate \( K = 5kPa \). Additionally, we measure the shear modulus rheologically and find it to be \( G' = 7.2kPa \), syneresis is inhibited due to adhesive walls of the rheometer. It should be noted that the Poisson’s ratio, \( \nu \), for this gel is unknown but assumed to be close to zero. As such, the mechanical relationship of

\[ K = \frac{2G(1+\nu)}{3(1-2\nu)} \]

becomes \( K \approx \frac{2}{3}G \) which is in excellent agreement with the measured values.

6.2.2 Gels composed of different particles types

After some time, the gel no longer contracts. While, syneresis is ubiquitous in gelled food products composed of liquid fat droplets, here, we observe syneresis is gels composed of rigid particles. To directly compare the magnitude of syneresis between different types of particles, we synthesize viscous droplets of polybutylacrylate, a low \( T_g \) polymer, of nearly an equivalent radius as the polystyrene. Additionally, we vulcanize these particles to form rubber particles [128]. From the polystyrene
particles, we grow a second lobe forming rigid dimers [129]. Again with a constant attractive strength due to the adsorbed surfactant, we syneresis these four different particle types at 45°C and measure the magnitude of syneresis, $\Delta \phi/\phi_0$ as a function $\phi_0$ after one day at temperature, as shown in Fig. 6.8. There appears to be two classes of particles: emulsion and rubber particles which syneresis dramatically approaching volume fractions equivalent to, or even exceed, random close packing, RCP, solid line in Fig. 6.8, and gels based on rigid polystyrene particles which arrest after moderate syneresis.

These four particle types have dramatically different stiffnesses, Young’s moduli, $E$. For emulsion droplets, $E_e = \sigma/R$ where $\sigma$ is the surface tension. The measured $\sigma = 8mN/m$ yields $E_e = 45kPa$. A simple force balance using the Young-Dupré equation and the measured adhesive energy, $0.5J/m^2$ from Fig. 6.2 at 45°C, results in a droplet-droplet contact angle of $\theta = 15^\circ$ [130]. Using optical microscopy, we measure the contact angle geometrically after finding the droplet centers and find $\theta$ to be substantially larger, $\theta = 29^\circ$; this discrepancy is most likely due to the difficulty in experimentally determining the surface tension of viscous liquids such as PBA. By contrast, the stiffness of rubber particles, $E_r$, is not only this capillary stiffness but also the polymeric elasticity due to the covalent crosslinks within the material; indentation tests such as those discussed later in Chapter 8 yield $E_r = 780kPa$. Consequently, the measured contact angle between rubber particles is small, $\theta \leq 2^\circ$; the upper bound here is dominated by noise in the imaging. Lastly, the stiffness of polystyrene, $E_p$, is taken to be the literature value of $E_p = 3GPa$; polystyrene-polystyrene particle contact angle is assumed to be negligible.
Figure 6.8: Magnitude of syneresis, $\Delta \phi / \phi_0$, for each particle type and initial volume fraction with ◇, rigid sphere, ▽, dimer, ◆, rubber sphere, and ▼, emulsion. Solid black line is equivalent to $\phi_{RCP} = 0.64$, and dashed line $\phi = 1$. 

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The interparticle contact angle geometrically determines the upper bound on the final packing fraction, $\phi_f$; emulsion particles being the most deformable could reach, $\phi_f \sim 0.90$, assuming monodisperse and ordered packing [131]. However, $\phi_f$ is never reached after one day; these gels also arrest. Additionally, both emulsion and rubber particles appear to undergo the same syneresis magnitude despite different contact angles and thus $\phi_f$, but still much more so than rigid particles, as seen in Fig. 6.8.

### 6.2.3 Cyclic syneresis

To elucidate this arrest further, we dynamically oscillate between a cohesive and repulsive interparticle potential by cycling the temperature above and below the LCST of the pNIPAm surfactant. The gels synereses, arrests after several hours, and then crucially, we remove the expelled fluid. As the sample cools, the gel relaxes and the interparticle potential becomes repulsive. At volume fractions below RCP, a fluid dispersion of particles is obtained; the mean diameter of these particles is still equivalent to the initial diameter as measured using dynamic light scattering, further emphasizing the lack of droplet coalescence or irreversible aggregation between rigid spheres. As the dispersion is heated again, the material synereses additional fluid is expelled; the process is repeated for a total of six cycles with the volume fraction after the end of each cycle being recorded, as shown in Fig. 6.9. Interestingly, the emulsion and rubber particle gels initially have a nearly identical volume fraction increase, but deviate at higher cycle numbers due to the deformability of the emulsion particles and their larger $\phi_f$. However, the previously calculated value in $\phi_f$ is still not obtained, most likely due to a lack of ordered packing as no opalescence is seen in
the dense emulsion. Likewise, freeze-fracture SEM imaging shows no ordering within the sample. By contrast to the emulsion and rubber particles, both the polystyrene and dimer gels slowly increase in $\phi$ but then plateau as the cycle number increases.

While $\phi_f$ is different for the emulsion and rubber particles, the similarity in initial increase of $\phi$ at low cycle numbers indicates a common syneresis mechanism not present in rigid particle syneresis. The surfaces or both emulsion and rubber particles are fluid with the surfactant diffusing laterally along the interface; rubber particles may be thought of as crosslinked liquids. We hypothesize that it is this surface mobility which allow these ‘soft’ particles to arrest only after obtaining a high $\phi$. A higher surface mobility would allow individual particle to slide relative to one another with near zero energy cost. By contrast, rigid particle gels with a low surface mobility arrest due to surface asperities; this is exemplified by the topological constrains in dimer dispersions. Arrest in emulsion and rubber gels is therefore likely a consequence of network connectivity; the gel contracts until further contraction would require the breaking of an interparticle bond which is energetically difficult as $U(k_BT) \sim 50$.

### 6.2.4 Stress bearing

In the absence of syneresis, the gel forms and elastically bears stress by either bending of strands or stretching of individual interparticle bonds, an increase in the center to center distance between particles. It should be noted that bending involves stretching of the bonds at the strand periphery. For centrosymmetric interparticle potentials such as polymeric depletion or this surfactant induced attraction, the energetic cost of relative particle rotation and therefore bending should be near zero,
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Figure 6.9: Cyclic syneresis; $\phi$ after a single syneresis cycle with $\circ$, rigid sphere, $\triangledown$, dimer, $\circ$, rubber sphere, and $\triangledown$, emulsion. Free expelled fluid is removed after each cycle.
but once the gel strand become ‘thick’ with a cross-section of more than one particle, bending may become appreciable. As the initial volume fraction in a gel increases, the thickness of a strand also increases for a constant attraction strength and shear history, see Chapter 5 for more information. The scaling of the gel elastic shear modulus, $G'$, with $\phi_0$ is a bulk measurement of the gel topology and thus a measure of how the gel bears any applied stress. In a rheometer, we form gels by heating the dispersion, syneresis is eliminated due to adhesive walls. For the four different particle types, the normalized elastic modulus, $\tilde{G}$, is measured for different $\phi_0$, where

$$\tilde{G} = G'(\phi)/G'(\phi = 0.3),$$

as seen in Fig. 6.10. For $\tilde{G} = (\phi - \phi_c)^\nu$, low powers of $\nu \sim 1.7$ are indicative of gels bearing stress by stretching interparticle bonds; by contrast, higher powers, $\nu \sim 3.3$, are indicative of gels bearing stress by bending network strands [132, 73]. Both mechanisms are not exclusive; often, the scaling exponent lies between these two extremes. We observe an increase in $\nu$ from dimers, to emulsions, to rubber, and lastly to polystyrene with a constant $\phi_c = 0.015$, particle radius, and interparticle attraction, as seen in Fig. 6.10. These results are intuitively consistent with previous assumptions about interparticle sliding: Particle types which permit sliding predominantly bear stress by stretching, whereas particle types with lower sliding bear stress by bending. Interestingly, the colloidal dimer gels show the lowest exponent, implying stress bearing by stretching; this is inconsistent with dimers imposing topological constraints which do not allow sliding. However, if sliding is nonexistent in these networks, gel strand cross-section thickness is likely only a single particle; these thinly stranded networks have very low bending moduli and therefore bear stress primarily by stretching.
Figure 6.10: Scaled elasticity, $\tilde{G}$, with $\phi_0 - \phi_c$ where $\phi_c = 0.015$ for ◦, rigid sphere, ▼, dimer, ●, rubber sphere, and ▲, emulsion. Scaling exponent varies from 1.5 to 2.4.
6.2.5 Section summary

In this section, we have shown that colloidal gels syneresis when the adhesive boundary conditions are eliminated and the gel forms in situ. Interestingly, we observe that the magnitude of syneresis is highly dependent on the type of particle used with the local deformability determining $\phi_f$. However, all gels arrest before reaching $\phi_f$; this arrest is attributed to the inability of the endogenous network stress to break an interparticle bond and thus change connectivity. We overcome this kinetic arrest by cycling the attractive potential allowing the network to freely rearrange, explore new configurations, and then inducing the attraction again; by doing so the gel approaches $\phi_f$. Gel networks which permit interparticle sliding reach $\phi_f$ within fewer cycles as more local lower energy states may be explored before global arrest. Likewise, these networks predominantly bear stress by stretching interparticle bonds not bending. While syneresis is more readily seen in 'soft' particle gels, it is not negligible in gels composed of rigid particles. Global syneresis is often not observed experimentally due to adhesive container walls. However, local syneresis within the network may still occur and be falsely interpreted as 'aging', where individual particle come off and on strands, in the literature\cite{4, 77, 133}.

6.3 Experimental for this chapter

All materials are purchased from Sigma-Aldrich and used as received, unless otherwise noted: 1-octadecanethiol, 2,2'-azobis(2-methylpropionitrile) (AIBN), ammonium persulfate (APS), carbon tetrachloride, chloroform, decane (99%), hexamethyldisi-
lazane (HMDS), nile red, N-isopropyl acrylamide (TCI America), poly(diallyldimethyl ammonium chloride) (PDADMAC) solution 20wt% (Mw \sim 400-500kDa), poly(sodium 4-styrenesulfonate) (PSS) solution 30wt% (Mw \sim 200kDa), polystyrene (Mw \sim 200kDa), rhodamine B, sodium chloride (NaCl), sodium styrene sulfonate, styrene (99%) and tetrahydrofuran (THF, anhydrous, 99%).

### 6.3.1 pNIPAm surfactant synthesis

The PNIPAm-C18 surfactant is prepared by free radical chain transfer polymerization. In a 500ml round bottom flask, 3.4g 1-octadecanethiol (11.8mmoles), 100g NIPAm (885mmoles) and 3.8g AIBN (23.6mmoles) are dissolved in 200ml of THF; the reaction ratios of thiol:NIPAm:AIBN are 1:75:2. The reaction is bubbled with Argon for 15 minutes and heated to 55°C overnight. The product is purified by precipitated into hexanes from THF, this is repeated twice and dried under vacuum. The molecular weight of the surfactant is characterized by GPC with THF as the running solvent; \( \langle M_w \rangle = 5200, \text{PDI} = 2.0 \).

### 6.3.2 Atomic Force Microscopy

We use colloidal probe atomic force microscopy (CP-AFM) to directly measure the interaction forces between pNIPAm surfactant covered surfaces, as a function of temperature. All force measurements are carried out using a Nanoscope 3 AFM (Digital Instruments), equipped with a PicoForce scanner. We glue a negatively charged sulfate modified polystyrene particles (Invitrogen, \( 2r = 8.6 \mu m \)) as a colloidal probe to a triangular, standard, contact-mode AFM cantilever (spring con-
constant, $k = 0.1325 \text{Nm}^{-1} \pm 0.007$) using NOA61 (Norland Adhesives). We confirm that a single particle is attached to the cantilever before and after experiments with optical microscopy as shown in the inset in Fig.1b inset. The bottom substrate for interaction measurements is prepared by spin-coating a thin layer of linear polystyrene dissolved in chloroform (1wt%) onto a clean silicon wafer pretreated with HMDS using a Laurell WS-650-23 spin-coater.

After placing the modified substrate and AFM cantilever in a sealed liquid flow cell, a concentrated (5g/L) surfactant solution is introduced to coat the surfaces with the thermoresponsive surfactant through adsorption. To ensure good coverage, we heat the entire cell to 45°C, hold for 15 minutes, lower the temperature to below the LCST and flush the system with the experimental solution in which we perform all our measurements, 0.05 gL$^{-1}$ pNIPAm surfactant solution in 100 mM NaCl. Force
distance curves are measured using a scan range of 0.35\(\mu m\) with scan rates ranging from 20 to 100\(nms^{-1}\) maintaining a contact time of 10sec between the probe and surface by varying the surface delay over a temperatures range from 27.0 to 40.0\(^\circ\)C. Additional force distance curves are collected at a fixed approach and retraction velocity of 100\(nms^{-1}\) while varying the contact time from 1s to 50s. We record at least 15 independent curves per temperature, scan rate and contact time. The peak force is found by normalizing the large separation force of each curve to zero and locating the minimum.

### 6.3.3 Bulk characterization

We use several techniques to characterize the bulk dynamic processes as stable colloidal dispersions are heated above the LCST of the adsorbed pNIPAm-C18 surfactant. Colloidal particles are synthesized using surfactant-free polymerization: in a sealed 1L round bottom flask equipped with an overhead paddle stirrer, 600ml deionized water and 60ml styrene are heated to 75\(^\circ\)C and bubbled with nitrogen for 15 minutes after which 0.6g APS predissolved in 7ml water is injected. The reaction proceeds for 36hrs. The resulting polystyrene colloids (2\(r = 0.436\mu m\), for distribution see Fig.6.12, SEM, Zeiss Supra 55) are washed into 1wt% pNIPAm-C18 solution by centrifugation. To ensure good coverage, the temperature is raised to 40\(^\circ\)C during the final centrifugation cycle. The dispersion is washed into the the experimental solution in which we perform all our measurements: 0.05 gL\(^{-1}\) pNIPAm surfactant solution in 100mM NaCl with 52vol\% \(D_2\)O to match the density of the dispersed phase to the polystyrene colloids. Oscillatory rheology is performed on an Anton Paar 501
rheometer using a double-walled Couette geometry applying a strain of 0.2% at 1Hz with a fixed heating rate of 0.5°C/min. A preshear of $\gamma = 200s^{-1}$ is performed between different temperatures (Fig. 6.3c); no preshear is performed during temperature cycling (Fig. 6.3d).

### 6.3.4 Colloidal synthesis and 2D microscopy

We use fluorescence microscopy to visualize the flexibility of individual bonds between colloidal particles. Fluorescently labeled $2r = 1.4\mu m$ polystyrene colloids are synthesized using dispersion polymerization [59]. The following are added to a 200ml round bottom flask: 47.2ml methanol, 8.4ml water, 10.0ml styrene, 200mg AIBN and 50mg sodium styrene sulfonate (stabilizer). The reaction is heated to 80°C under reflux for 8hrs. The suspension is filtered and washed by centrifugation (3X) into 1wt% pNIPAm surfactant to $\phi \sim 10\%$. To fluorescently labeled this dispersion, the particles are swollen with an aqueous miniemulsion of carbon tetrachloride ($\phi \sim 10\%$), containing dissolved fluorophore (nile red), stabilized by 1wt% pNIPAm surfactant. The total carbon tetrachloride volume is 50vol% to that of particle solids. This miniemulsion is added to the suspension of particles and stirred for at least 24hrs. Nitrogen is blown over the solution at 50°C for at least 6hrs to evaporate the plasticizer (carbon tetrachloride). Free dye is removed from the colloidal dispersion by repeated centrifugation and redispersion in a 0.05gL$^{-1}$ pNIPAm surfactant solution with 100mM NaCl.

2D microscopy imaging chambers are prepared with a polyelectrolyte multilayer (PEM) to ensure that colloids do not adhere to the chamber at temperatures above
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Figure 6.12: Calculated particle size distribution from several SEM images.

Precleaned coverslides and coverslips are repeatedly immersed in 1wt% pDADMAC in 2M NaCl, rinsed with deionized water, 1wt% pSS in 2M NaCl, then rinsed, for a total of 6 polymer layers ending with an anionic PSS layer. A nearly 2D imaging volume is achieved by using adding a very small volume of the colloidal dispersion (1µL, φ ~ 5%) to a PEM treated coverslide, sealing the chamber with a PEM treated coverslip and 5-minute epoxy.

High speed 2D imaging experiments are carried out on a low volume fraction suspension (φ ~ 0.05 in 100mM NaCl) using a Leica SP5 confocal microscope (100X oil objective) with a heated stage (Warner Instruments, WP-10) at 40°C. Several thousand of images are captured at 50, 5 and 0.5 frames per second and precise particle locations found using standard centroid tracking algorithms. For Fig.6.4, (a) the pinhole is set to 3.0 airy units, (b) the pin hole is reduced to 0.5 airy units.
Confocal microscopy

We use confocal microscopy to visualize phase inversion of an oil in water emulsion stabilized by the pNIPAm-based surfactant. Experiments are carried out on a Zeiss Axiovert 200M microscope with objective and stage heaters (Warner Instruments, OW-1, WP-10). The emulsion is prepared at $\phi = 20\%$ decane in $1\text{gL}^{-1}$ surfactant solution, with a trace amount of rhodamine B, by homogenization. The emulsion is allowed to cream over several hours and a small volume at high volume fraction ($\phi \sim 65\%$) imaged at $22^\circ\text{C}$, heated to $40^\circ\text{C}$, then cooled to $22^\circ\text{C}$ over $\sim 30$ minutes in total.
Chapter 7

Chemically induced coalescence in droplet-based microfluidics

The Weitz laboratory is a highly diverse research environment encompassing chemistry, biology, and physics. While a member of the laboratory, I have primary worked in the sub-area of colloids research but I have had the opportunity to work on a rich variety of projects outside this sub-area, particularly in the development of microfluidic techniques. This Chapter and the subsequent Chapter discuss these projects and their results.

7.1 Chemical coalescence

Droplet microfluidics is a promising approach for high-throughput combinatorial biological and chemical assays: Each water droplet dispersed in an inert carrier fluid, typically fluorocarbon oils, acts as a small volume microreactor [134, 135, 136, 137,
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Droplets, ranging in volume from a few picoliters to nanoliters, can encapsulate aqueous reagents and isolate their contents \[139\]. For long-term compartmentalization of active compounds in droplets, surfactants are added to prevent coalescence. To perform such biological assays, reagents must be mixed with the contents of each individual droplet; this may be achieved through coalescence, whereby a sample droplet is paired and merged with a droplet containing new material \[140\].

However, as this biologically inert oil-water interface is nearly always stabilized with surfactants, such targeted coalescence becomes challenging. Several experimental methods have been developed to locally bias this competition between surfactant driven stability and controlled coalescence. Partially stable droplets with a minimal surfactant concentration have been coalesced using abrupt changes in surface area \[141, 142\]. By contrast, coalescence of fully stabilized droplets has only been achieved using external stimuli: electro-coalescence and optical heating \[140, 143, 144, 145, 146\]. Electro-coalescence of droplets involves merging of droplet pairs by applying an electric field as droplets pass through a confined region of a microfluidic channel bordered by fabricated electrodes. Optical heating of droplet interfaces involves using a focused laser to locally change the temperature and the surface tension of the droplet interfaces. These methods are complex and the development of a simple and robust method for performing controlled droplet coalescence would be beneficial.

In this chapter, we present a new microfluidic method to coalesce a stream of paired surfactant-stabilized water-in-fluorocarbon oil droplets. The local addition of a poor solvent for the surfactant, perfluorobutanol, induces cohesion between paired
Figure 7.1: Passive microfluidic droplet coalescence through the addition of a destabilizing alcohol; the flow direction is from left to right. (a) Upstream pairing of two different size droplets labeled with Rhodamine-Dextran (red, small) and Fluorescein-Dextran (green, large). (b) Perfluorobutanol is added through the channel indicated by the black arrow, causing downstream coalescence of paired droplets.

droplet interfaces, the droplets merge and coalesce. Then the alcohol is diluted to restabilize the droplets. To elucidate the mechanism that leads to coalescence, we determine the surfactant solubility and, by measuring the static interfacial tensions and the droplet contact angles at different proportions of alcohol, we determine the strength of the cohesion between droplets. We show that the merging efficiency of this chemical coalescence method is comparable to electro-coalescence of droplets.

To coalesce a bulk emulsion of aqueous droplets in fluorinated oil, a concentration of 20vol% perfluorooctanol, PFO, is typically used \cite{147}; however, breaking the emulsion requires a combination of vigorous mixing and centrifugation. Instead, we use perfluorobutanol, PFB, which results in bulk coalescence with no mixing or centrifugation. Eliminating the necessity for mechanical agitation provides a path where a sample droplet can be passively coalesced with a second droplet containing new reagent inside a microfluidic channel.

For this chemically induced merging, we use a flow focusing geometry to produce 40µm droplets, labeled green, while simultaneously reinjecting pre-formed 25µm
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droplets, labeled red. Each droplet stream enters one side of a Y-junction as shown in as seen in Fig. 7.1a [148]. Synchronization between droplet streams is achieved by controlling the flow rate of each stream using syringe pumps. Synchronization is reinforced due to a small pressure fluctuation as the larger droplets enter the exit channel, forcing the reinjected smaller droplets to slow down and then follow the large droplet out the exit channel of the Y-junction [138]. Once synchronized, the droplets must touch, or pair. A long straight channel is added after the Y-junction to allow the smaller droplets to catch up to the larger droplets; the smaller droplets sample less of the flow profile and thus experience a higher average velocity [140]. Successfully paired droplets may now be coalesced.

7.1.1 On-chip coalescence

However, for this on-chip chemically-mediated coalescence to occur, paired droplets must interact with an incoming PFB stream. Fluid additions at low Reynolds number, as in microfluidic devices, will divert streamlines and push droplets away from any incoming stream, see Fig. 7.4. To steer droplets across streamlines to the lower wall where the PFB is introduced from a side channel, we modify the long straight channel. By adding an 8µm tall tapering feature to the channel ceiling, buoyant aqueous droplets fill this additional volume and are steered by the taper to the lower channel wall as seen in Fig. 7.2a. By contrast, in a simple rectangular cross-section channel, droplets remain centered as shown in Fig. 7.2b. We quantify the steering by measuring the center of each droplet as it flows along the microfluidic channel as shown in Fig. 7.2c; the droplet centers move 8µm toward the lower wall and the
Figure 7.2: Droplets steering channel. (a) Droplets passing through a 50 \( \mu \text{m} \) wide, 25 \( \mu \text{m} \) tall microfluidic channel with a tapering 8 \( \mu \text{m} \) tall feature added on the ceiling. (b) Droplets passing through a rectangular 50 \( \mu \text{m} \) wide, 25 \( \mu \text{m} \) tall channel. A schematic of the channel cross-section is shown at right, with the droplet volume represented in blue. Scale bar is 150 \( \mu \text{m} \). (c) Average droplet center position in the channel as a function of droplet position along the flow direction; (○) without steering-ceiling, (●) with steering-ceiling. 0 on the y-axis corresponds to the channel center-line.

Incoming PFB stream.

Droplet pairs now exit the steering channel and directly contact a stream of PFB for \( \sim 1.30 \text{ms} \), as shown by black arrows in Fig. 7.3a-c. The paired droplets pass through a constriction in \( \sim 2.6 \text{ms} \) as shown in Fig. 7.3d-g; upon exiting, the velocity of the leading green large droplet rapidly decreases in <0.5ms, forcing the droplet pairs into close contact and then to quickly coalesce, as shown in Fig. 7.3h-i. Once coalesced, the single yellow droplets flow downstream where the PFB is diluted with continuous phase added through the large side channel shown in Fig. 7.1b. No more coalescence events are seen after this dilution. We simply collect the merged droplets off-chip for additional steps. This entire process proceeds at approximately 300 droplet merging events per second, comparable to the rates of electro-coalescence methods [136, 138, 140]; the complete device drawing is shown in Fig. 7.9.
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Figure 7.3: A time sequence of droplet pairs contacting an incoming PFB stream (a-c), passing through the constriction (d-h) and coalescing (i). Wall adhesion is marked by black arrows. Droplets are false colored.
Interestingly, as paired droplets contact the stream of undiluted PFB, they appear to adhere strongly to the channel wall as indicated by black arrows in Fig. 7.3. Coalescence between drops occurs rapidly once the surfactant-stabilized droplets touch each other due to this adhesion. Here, we use a flow rate of 10 $\mu$L/hr of PFB; this stream is barely visible in Fig. 7.3. If all flows were fully mixed, the resulting concentration of PFB would be 1vol% in the continuous phase. However, when the droplet pairs first contact PFB, the local concentration is far higher than the fully mixed concentration, yielding a high concentration gradient which enhances local adhesion. At higher flow rates of PFB, and thus $>1$vol% fully mixed concentrations of PFB, we are no longer able to collect stable singly-coalesced droplets at the device outlet. This agrees with bulk experiments performed in a vial: The onset of bulk coalescence occurs at $\sim2$vol% PFB. Surprisingly, adhesion and coalescence are absent when PFO is flowed instead of PFB in the microfluidic device operation described above, regardless of flow rate. Similarly, adding fluorocarbon oil instead of PFB yields no coalescence events; device

Figure 7.4: Fluid streamlines for operational flow rates in the merging microfluidic geometry generated by computation fluid dynamics in COMSOL. Flow rate for PFB addition are (a) 5ul/hr and (b) 100ul/hr.
geometry alone is insufficient to account for the adhesion or coalescence [130]. Clearly, the interaction between the PFB and the paired droplets is playing a crucial role in the observed adhesion and subsequent coalescence.

7.1.2 Surfactant adsorption and interfacial tension

To understand the effects of PFB on the surfactant-laden interface, we characterize the interface of the water-in-oil emulsion by measuring interfacial tensions for the local conditions encountered in the microfluidic system. We determine the interfacial tension for different surfactant and bulk alcohol concentrations using both pendant drop and DuNuoy ring techniques. At low surfactant concentration, 0.1 mM, $\gamma$ decreases exponentially until a very low value is reached as seen in Fig. 7.5a. By fitting this kinetic equilibration of the surface tension to a simple exponential function, we determine a time constant, $\tau$, for surfactant adsorption to the interface. Surfactant loading to the interface is predominantly a diffusion driven process where there is an equilibrium between adsorbed surfactant and micellar surfactant. The surfactant used in these experiments is peculiar; irregardless of the initial concentration, $\gamma$ always greatly decreases to $\Delta \gamma > 20mNm$ and the pendant drop frequently pinches off. This appears to imply that once adsorbed it does come off the interface. Therefore by measuring $\gamma$, we are strictly measuring the adsorption rate to the interface. Above a certain concentration, surfactants assemble into micelles; the concentration being the critical micelle concentration or CMC. We measure $\tau$ for different surfactant concentrations and find a plateau at high concentrations as seen in Fig. 7.5b. This concentration at which we enter the plateau region corresponds is equivalent to the
Figure 7.5: Dynamic and equilibrium interfacial tensions as a function of alcohol concentration. (a) Dynamic interfacial tension (gray points) and corresponding exponential fit (black line) for a water droplet in HFE-7500 oil with 0.4wt% surfactant. (b) Time constant from exponential fits for several PFB concentrations: (●) 0vol%, and (○) 0.1vol%; at 1vol% relaxations occurred faster than measurable. (c-d) Equilibrium interfacial tension, $\gamma_0$, from pendant drop and DuNouy ring measurements as a function of perfluorobutanol (PFB) or perfluorooctanol concentration; (●) 2wt% surfactant, (○) no surfactant.
CMC as micelles adsorb at a constant rate whereas individual molecules must diffuse to the interface. After equilibration and without surfactant, increasing PFB volume fraction causes an abrupt decrease in the interfacial tension from that of the clean water-fluorinated oil interface, $\gamma=32\text{mN/m}$ to $\gamma=15\text{mN/m}$ at only 2vol% as seen in Fig. 7.5c. Similarly, adding 2wt% surfactant to the bare interface in the absence of PFB also results in a large decrease in the interfacial tension, $\Delta \gamma \sim 30\text{mN/m}$; a change of this magnitude indicates a very dense packing of surfactant molecules \[149\]. Interestingly, upon addition of PFB to this surfactant-laden interface, the interfacial tension rises sharply at 2vol% PFB approaching the value for the surfactant-free interface as seen in Fig. 7.5c. At concentrations >5vol% PFB, the interfacial tension difference between surfactant-free and surfactant-laden interfaces appears to be zero; suggesting that at these PFB concentrations the surfactant no longer stabilizes the interface. This effect is completely absent for identical measurements made with PFO: The interfacial tension difference for surfactant-free and surfactant laden interfaces is not zero until >50%vol PFO as seen in Fig. 7.5.

To resolve this stark contrast in interfacial behavior between two seemingly similar alcohols, we examine the bulk phase equilibrium of fluorocarbon oil with 2wt% surfactant at different concentrations of PFB and PFO. Once the oil phase reaches 85vol% PFB, the sample becomes turbid as the surfactant precipitates out of solution. By contrast, the surfactant is soluble at 2wt% at all concentrations of PFO. Crucially, it is this precipitation that causes the cohesive nature of surfactant-stabilized droplet interfaces. By locally adding a poor solvent for the surfactant, we are able to induce cohesion between fluid interfaces causing rapid draining of the thin liquid film.
between droplets and rendering the interfaces highly susceptible to shear and coalescence [130, 141].

7.1.3 Confocal measurement - adhesion and contact angle

This cohesion is first seen as adhesion to the microfluidic channel walls which are coated with surfactant as seen in Fig.7.3. We quantify the strength of adhesion between surfactant-coated surfaces by measuring the contact angle made by a single droplet with a surfactant-coated PDMS surface using 3D confocal microscopy as schematically shown in Fig.7.6a. Imaging a fluorescent aqueous droplet labeled with FITC-dextran at the droplet equator yields the droplet diameter as seen in upper im-
Simultaneously, we measure the diameter of the adhesive contact area using confocal reflection microscopy where a dark patch appears at the PDMS-droplet interface, akin to black spots in thin films as seen in lower images of Fig. 7.6B. Using these two diameters, the adhesive contact angle, $\theta$, is calculated geometrically and shown as a function of alcohol concentration in Fig. 7.7a. Combined with the previously measured surface tensions, $\gamma_0$, we calculate the energy of adhesion, $\Delta F$, as a function of alcohol concentration according to $\Delta F = 2\gamma(1 - \cos(\theta)) \ [150]$. We find that the energy of adhesion for interfaces exposed to PFB, increases around 5vol% as seen in Fig. 7.5b. By contrast, the energy of adhesion for interfaces exposed to PFO becomes non-zero only at concentrations $>50$vol%. Both results are in excellent agreement with a cohesion-based coalescence between droplets for PFB, and the surfactant remaining soluble at all concentrations of PFO.

While 5vol% PFB is required to induce cohesion and coalescence of a single droplet
Multiple downstream coalescence events must be prevented for microfluidic assays. We achieve this by reducing the concentration of PFB; droplet interfaces are restabilized by eliminating the cohesion. After a single droplet pair coalescence event, we introduce a new stream of PFB-free continuous phase in the microfluidic device, lowering the final PFB concentration to \(<1\text{vol}\%\). By diluting the PFB, merged and then restabilized droplets are able to be collected from the device outlet continuously for up to 7 hours.

To determine the efficiency of this chemical coalescence process on the microfluidic chip, we count droplet merging events recorded in high-speed movies. If drops are successfully paired, greater than 96\% are successfully merged; this is nearly as efficient as electro-coalescence of droplets \([138, 140, 145]\). However, undesired coalescence events between more than two droplets often occur. These ‘extra’ droplets are typically a result of imperfect upstream pairing; an excess number of small droplets may enter the coalescence region of the device with a droplet pair, forming a triplet.
We observe that the oblate post in this microfluidic device diverts most of the single droplets to the top channel away from the constriction zone, avoiding triplets. Additionally, when three droplets do enter the constriction region of the device, we do not observe all three droplets coalescing; such events are inherently prevented as all three droplet interfaces must be in contact for chemical coalescence to proceed. By contrast, as the electric field interaction in microfluidic electro-coalescence is long ranged compared to the size of a droplet pair, multiple droplets may be driven together and coalesced [138, 140].

### 7.1.4 Chapter summary

In this work, we report a method to coalesce droplets through the local addition of PFB, yielding interfacial cohesion between surfactant-stabilized droplet pairs in a microfluidic device. This new tool for coalescing otherwise perfectly stable droplets inside a microfluidic device is an alternative to the use of electric fields [138, 140, 143, 145] and optical heating [146]. The absence of electric field may be beneficial for certain biological assays where electroporation [151, 152] or cell lysis [153, 154] of mammalian cells must be avoided. This method simplifies on-chip droplet coalescence as it requires no electrodes or additional instrumentation such as the electronics to control electrodes or the sensitive alignment of lasers.

### 7.1.5 Experimental for this chapter

Microfluidic channels are fabricated in poly(dimethylsiloxane) (PDMS) using standard soft lithography protocols [43, 155]. The fluidic channel mold is fabricated via
photo-lithography and chemical development of SU-8 photoresist (Microchem). Sylgard 184 PDMS (Dow Corning) is mixed at the standard 1:10 mass ratio, poured over the mold, degassed for 20 minutes under vacuum, and cured at 65°C for 18 hours. After curing, the PDMS replica is removed from the mold, fluid inlet holes formed with a biopsy punch, and the PDMS piece bonded to glass using oxygen plasma treatment \[156\]. The microfluidic channels are treated with a fluorophillic silane, Aquapel (Ryder Fleet Products) is flowed through the channels for 30 seconds, and then flushed out with Novec HFE-7500 (3M) fluorocarbon oil.

Unless otherwise noted, the dispersed phase for all experiments is DI water. The continuous phase is Novec HFE-7500 with additional components, as noted. Aqueous droplets are stabilized using 2wt% PFPE-PEG-PFPE triblock copolymer surfactant \[157\] dissolved in the fluorocarbon continuous phase, at roughly 2.5x times the CMC. 2,2,3,3,4,4,4-Heptafluoro-1-butanol (PFB, Oakwood Products) is used to induce droplet coalescence.

Prior to a droplet coalescence experiment, one droplet population is formed in a flow-focusing design microfluidic channel with a droplet nozzle cross-section of 15 μm x 15 μm. 25 μm droplets are created using flow rates of 180 μL/hr and 100 μL/hr for the continuous and dispersed phases, respectively. Droplets are collected into a 1 mL plastic syringe (Becton Dickinson). These droplets are used as the reinjected droplet population during coalescence experiments.

Droplet coalescence experiments are performed using the Y-channel. From the lower arm of the Y, we inject 25 μm droplets at 15 μL/hr and space them with HFE-7500 flowing at 150 μL/hr. From the opposite arm of the Y, 40 μm droplets
are formed at a flow-focusing nozzle using a dispersed phase flow rate of 40 µL/hr and a continuous phase flow rate of 300 µL/hr. In the coalescence region of the device, 100% PFB is injected into the continuous phase at 10 µL/hr. Coalesced droplets are restabilized by adding fresh HFE-7500 at 500 µL/hr to dilute the final PFB concentration. See Figure 7.9 for complete device drawing.

Interfacial tension measurements are performed on two instruments. Equilibrium measurements are made on a KSV Sigma 701 tensiometer (Biolin Scientific) with a platinum DuNouy ring; the ring is rendered fluorophilic by silanization in 1vol% 1H,1H-2H,2H-perfluorodecyl trichlorosilane (Sigma) in HFE-7500. Dynamic and equilibrium measurements are also made using a custom pendant drop instrument. The pendant drop instrument captures digital images at frames rate up to 15 fps and calculates the interfacial tension values using a curve fitting route in Matlab to match the droplet interface profile [158, 159]. Values from this pendant drop instrument are verified against values calculated by a commercial KSV CAM 200 pendant drop surface tension meter (Biolin Scientific).

Adhesion measurements are performed in droplet imaging chambers. The chambers are fabricated by sandwiching 1 mm thick glass spacers between a standard microscope slide and a glass coverslip coated with cured Sylgard 184. This sandwich is glued together using NOA 81 (Norland Products, Inc) and exposed to UV to cure. Chambers are immersed in Aquapel, dried with compressed air, and then soaked for 5 minutes in a solution of 2wt% PFPE-PEG-PFPE in HFE-7500 to guarantee surfactant coating the interior of the chamber. The chamber is then removed from the surfactant solution, dried with compressed air, and all but one side sealed using
5-minute epoxy. Once the epoxy is cured, the chamber is filled with the appropriate test solution, then droplets containing 0.5 mg/mL dextran-Fluorescein are pipetted into the test solution. Adhesion is quantified by recording simultaneous XYZ image stacks of the fluorescence and laser reflection signals.

**Coalescence performance: a fluorescence assay**

Fluorescence assay experiments (see Fig. 7.10) are performed by encapsulating dextran labeled with Rhodamine B (Mw~70kDa, Sigma-Aldrich) and dextran labeled with Fluorescein (Mw~70kDa, Sigma-Aldrich) in droplets and characterized by confocal microscopy (Leica SP5). The time stability of fluorescence assay droplets are done by storing the collected droplets in closed vials for three days and imaging the droplets on confocal microscopy at 24, 48, and 72 hours.
Figure 7.9: Complete device drawing.
Figure 7.10: Two-color overlay fluorescence images of droplets collected from the outlet of the microfluidic device using: (a) HFE-7500, (b) PFO, and (c) PFB; scale bar is 150mm. 2-D histogram of all individual droplet fluorescence intensities obtained from coalesced droplet pairs in (d) HFE-7500, (e) PFO, (f) PFB.
Chapter 8

Siloxane chemistry and Soft Matter

Polydimethylsiloxane, PDMS, is a highly versatile polymer for many applications within soft matter. PDMS has an extremely low glass transition temperature, $T_g = -125^\circ C$, which allows the polymer to stay fluid-like, almost never glassy. Siloxane solvent interactions are often overlooked, while hydrophilic and lipophilic interactions are the most common, there is also fluorophilic and silanophilic; the latter being mostly frequently associated with PDMS polymers. PDMS is not miscible with water, mineral oil, or fluorinated chemicals [160]. These additional immiscible siloxane combinations allows microfluidics to be tractable as a research field; glass microfluidics is considerably more inflexible yet non-scalable and limited to laboratory not industrial application. Not only scientifically, PDMS is extremely commercially valuable; siloxanes are used in home and personal care product including makeups, shampoos and lotions as well as countless industrial applications from lubricants to heat-exchange fluids. As a result PDMS chemistry has been extensively investigated within the chemistry community with many chemically useful variants being commercially avail-
able and inexpensive. In Chapter 2, we used a mono-methacrylate terminated PDMS to synthesize a stabilizing comb polymer for PMMA colloids. Likewise, in Chapter 7, we used a formulated PDMS elastomer kit, Sylgard 184, to fabricate a microfluidic device with extremely high spatial precision and a high degree of functional use. In this chapter, we will explore further the application of siloxanes within soft matter. This chapter is divided into three sections; a diphenyl siloxane-based elastomer for use in microfluidics, a UV curable PDMS for use in microfluidic capsule generation, and lastly a non-linear PDMS polymer, a bottle-brush, which eliminates entanglements allowing soft PDMS elastomers.

8.1 Polydiphenylsiloxane elastomers and their use in microfluidics

Droplet formation in microfluidic devices made by conventional soft lithographic methods is limited to solvents which do not swell polydimethylsiloxane, PDMS. Swelling of the elastomer causes undesired wetting and changes in the channel cross-section; the result is droplet polydispersity and eventually clogging. In this section, we present a new elastomer based on polydiphenylsiloxane, PDPS, that does not swell in silicone fluids and exhibits stable droplet production over many hours. Silicone fluids as either the dispersed or continuous phase offer many advantages such as low cost, commercially available siloxane based-surfactants, and a large viscosity range.

PDPS, diphenyl siloxane is mostly immiscible with PDMS; by changing only 17mol% of dimethyl groups with diphenyl groups, a 1:1 volumetric mixture of PDMS:PDPS
Figure 8.1: (A) Macroscopic phase separation of linear polydiphenylsiloxane (PDPS) and polydimethylsiloxane (PDMS), (B) vinyl terminated PDPS, (C) multi-functional PDPS cross-linker, (D) hydrosilation reaction of the vinyl bond with the silicone hydride catalyzed by a Pt complex at elevated temperature (E) a typical device with several microfluidic droplet makers.
Figure 8.2: Kinetic swelling of three different siloxane elastomers: Dow 3-6121, Sylgard 184 and PDPS in silicone oils with different viscosities. ▲ Dow 3-6121 in 5 mPa·s, ◆ Dow 3-6121 in 20 mPa·s, ▲ Sylgard 184 in 5 mPa·s, ◆ Sylgard 184 in 20 mPa·s, △ PDPS in 5 mPa·s, ◊ PDPS in 20 mPa·s, and □ PDPS in 100 mPa·s.

phase separates into a 60:40 split as seen in Fig. 8.1a. Increasing the mole fraction of diphenyl groups does increase the steepness of the tie lines but in so doing also raises the $T_g$ of the copolymer close to room temperature [161]. Nearly all siloxane elastomer formulations contain five ingredients, our PDPS elastomer is no different: divinyl-terminated ‘base’ polymer, hydride functionalized ‘crosslinker’, platinum catalyst, silica nanoparticle solid filler, and liquid filler. The first 3 components are reactive with a hydrosilation scheme shown in Fig. 8.1b-d. Solid and liquid filler are added to increase the toughness and extensibility, respectively; the addition of nanoparticle silica filler results in the fabricated device possessing a blue hue due to Rayleigh scattering as seen in Fig. 8.1e.

By far the most common elastomer used in microfluidic devices is Sylgard 184.
Another commercially available elastomer is Dow 3-6162, which has a higher index of refraction suggesting some phenyl substitution. To compare the swelling difference between these two elastomers plus PDPS, a simple swelling test is adopted. 3 increasing molecular weights of silicone fluids are tested, corresponding to 3 viscosities 5, 20, and 100 mPa·s. In all cases, PDPS swells the least with a swelling ratio, $S \leq 0.1$ for all times as shown in Fig. 8.2. Sylgard and 3-6162 exhibited significantly greater $S$. While PDPS fairs well with silicone oils due to it’s immiscibility with PDMS, kinetic swelling in non-siloxane solvents is comparable to PDMS as seen in Fig. 8.3 [160]. Thus, PDPS offer only a significant advantage over PDMS when silicone oils are used as the continuous phase.

To show the performance of PDPS as a microfluidic device, we make a simple droplet maker operating with 20 mPa·s silicone oil as the continuous phase as seen in Fig. 8.4. The operation of the droplet maker over time becomes not ideal for both other elastomers as the channel dimensions change and there is uncontrolled wetting of the aqueous phase with the channel wall. The PDPS device operated for several hours with no measurable change in channel dimensions, while channel dimension for both Sylgard and 3-6162 decrease to the point of closure as seen in Fig. 8.5. Combined with readily available PDMS-based surfactants for water-in-oil emulsions, PDPS offers a simple and straightforward alternative to conventional elastomer kits.

8.1.1 Experimental for this section

We use commercially available materials from Gelest, Inc. unless otherwise noted: diphenyl-dimethylsiloxane copolymer (liquid filler, 18-22% diphenyl, PDM-1922), vinyl
Figure 8.3: Kinetic swelling of PDPS in solvents:  ★ chloroform, ✗ toluene, ♦ 5 mPa·s silicone oil, ● dimethylformamide, ▼ 1-octanol, ◈ 20 mPa·s silicone oil, □ dimethylsulfoxide and ▱ 100 mPa·s silicone oil.
Figure 8.4: Droplet production with different elastomers; droplet phase is water, continuous phase is 20 mPa-s silicone oil with 1wt% Dow 5225C, as surfactant.

Figure 8.5: Channel width measured at the dashed lines for 25μm droplet makers made from different elastomers as seen in Fig. 4. ●, PDPS, □, Dow 3-6121, ▼, Sylgard 184
terminated diphenylsiloxane-dimethylsiloxane copolymer (base, 15-17% diphenyl, Fig. 8.1b, PDV-1631), hydride terminated methyl-hydrosiloxane-phenylmethylsiloxane copolymer (crosslinker, Fig. 8.1c, HPM-502), hexamethyldisilazane treated fumed silica (solid filler, SIS6962.0, avg. diameter 20nm), platinum-octanaldehyde/octanol (catalyst, SIP6833.2) and diethyl maleate (inhibitor, Aldrich).

**Poly-dimethyl-diphenyl elastomer**

Polydiphenylsiloxane elastomer is prepared in two parts for long term storage. Part A is prepared by suspending 100 g of the solid silica filler in 350 ml hexane by sonicated for $\sim$12hrs. This slurry is transfer to an overhead mixer and while mixing at 40 s$^{-1}$, 430 g of the base is slowly added; mixing is increased to 100 s$^{-1}$ and held for $\sim$12 hours while air is blown over top the mixture to remove the hexane. Part A is stored as a $\sim$18% by weight silica dispersion with 500 $\mu$l of catalyst and 500 $\mu$l of inhibitor. Part B contains 29.2 g of liquid filler, 23.8 g of crosslinker, which are simply combined and stored at room temperature. A 10:1 mixture of Part A : Part B by weight ratio is prepared upon immediate usage. By mixing at this weight ratio, an equivalent mole ratio of hydride from the crosslinker to vinyl from the base, of 3.5 is obtained; for stronger elastomers increase this ratio to 9:1.

**8.1.2 Swelling measurements**

To test the swelling, or preferably lack of swell of the PDPS elastomer, we perform swelling test similar to [160]. $\sim$2g pre-weighted cube of PDPS elastomer are placed in large vials, a large excess of the respective test solvent is added to the vial and
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the vial tumbled for several days. The cube is removed, padded dry with a Kimwipe only to remove excess solvent, and the cube weighted. The change in mass along with the known density of the solvent allow us to calculate the swelling ratio, defined as $S = \log(m(t)/m(0))$. For instance a $S=1$ would be a 10 fold increase in the mass of the cube, density difference are not accounted for as only chloroform has an appreciable different density and is not the focus of this work.

8.1.3 Device fabrication and droplet production

Microfluidic channels are fabricated using standard soft lithography [43]. Briefly, fluidic channel molds are fabricated via photolithography of SU-8 photoresist (Microchem) and uncured elastomers cast over them. Following curing at 65°C for 18 hours, the elastomer replica is removed from the mold, inlet holes are formed with a biopsy punch, and the channels are bonded to glass using oxygen plasma treatment [156]. No surface treatment of the channels is performed. Unless noted otherwise, the dispersed phase for all experiments is DI water. The continuous phase is 20 mPa·s silicone oil with 1wt% Dow 5225C, as surfactant.

8.2 Microfluidic fabrication and micromechanics of permeable and impermeable elastomeric microbubbles

In this section, we use a UV curable PDMS prepolymer and droplet microfluidics to produce monodisperse elastomeric microbubbles consisting of gas encapsulated in a
PDMS shell. Microbubbles are spherical particles consisting of gas encapsulated in a shell. They are conventionally used as components in aerated food products, materials for energy storage and waste-water treatment, vehicles for drug delivery, and tools for contrast enhancement in ultrasound [162, 163, 164]. In addition, microbubbles are used as pressure probes for magnetic resonance imaging: their size change under applied pressure registers as a shift in the nuclear magnetic resonance signal intensity. This unique property enables their use as pressure mapping agents to study fluid flow in porous media [165, 166] and to map local pressure changes in oil reservoirs. To truly be useful in such confined geometries, microbubbles must be able to reversibly deform following their passage through confined porous space under high pressure conditions. Thus, a microbubble shell with the combined mechanical properties of high flexibility and resilience is required.

The mechanical properties of the microbubble shell can be altered by changing two aspects: chemical composition and thickness. Typically, shells are chemically composed of either lipids, which are flexible yet mechanically weak, or polymers, which tend to be rigid yet mechanically strong [167]. Increases in shell thickness always result in higher bending stiffness. Modification of such physical and chemical characteristics is not easily attained through conventional microbubble fabrication strategies. To circumvent this limitation, droplet microfluidics is used to control the physical properties of microbubble size and shell thickness by flow rate variation, and chemical composition by flexibility in choice of material [168, 169, 170, 171]. Shells that are both flexible and mechanically resilient are produced from elastomeric PDMS, commercially sold typically as a two-part curing system. The stiffness of PDMS is
adjusted easily by altering the ratio of the two-parts: base and cross-linker during the hydrosilation reaction. Successful tuning of these physicochemical properties may increase microbubble versatility and robustness.

Once fabricated, a number of available experimental techniques are useful for measuring the mechanical properties of microbubbles, such as AFM [172, 173, 174], micropipette aspiration [175], and parallel plate squeezing [176]. The latter technique measures the force required to squeeze spheres or shells between two rigid parallel plates while measuring the distance, or gap, between the plates [176]. These experimental compression tests are substantiated by non-linear numerical finite element analyses [177]. In addition, the numerical simulations enable a priori estimates of microbubble deformation extents. Despite the availability of experimental compressive and numerical analysis techniques, they have not been used to elicit variations in engineered microbubbles, fabricated through controllable methods such as microfluidics.

In this section, we use droplet microfluidics to prepare monodispersed elastomeric microbubbles with a PDMS shell. We measure the deformability of these microbubbles by conducting mechanical compression tests on individual microbubbles to obtain force-displacement curves; we then compare these results to finite element models. This enables the design and development of deformable microbubbles that have a predictable mechanical response.

### 8.2.1 Microbubble generation with microfluidics

Elastomer microbubbles are generated using a glass capillary microfluidic device: A cylindrical injection capillary and a collection capillary are co-axially aligned within
Figure 8.6: (a) Glass microfluidic device with inlets and outlets labeled. (b) Top panels: schematic illustration of the microuidic generation of bubbles stabilized by an unpolymerized PDMS shell, solid border (see a), which further downstream breaks into individual drops, dashed boarder (see a). Bottom panels: optical microscope images showing the emulsification process. Scale bar is 200 µm for all images. (c) Optical image of three monodispersed microbubble populations formed using a PDMS flow rate of 1.0, 1.5, and 2.0 ml/hr, from left to right; Scale bar is 200 µm for all images.
a square capillary \cite{178}. We use pressure-driven flow to drive a nitrogen gas stream into the injection capillary, and a syringe pump to drive the flow of the middle phase consisting of a PDMS monomer in the space between the square and injection capillaries; this yields the primary gas-in-oil emulsion. To obtain the final gas-in-oil-in-water double-emulsion, the primary emulsion is further emulsified by the syringe pump driven continuous phase, as shown in the schematic and optical image in Fig. 8.6a. Due to the high viscosity of the middle oil phase, breakup occurs downstream of the orifice where the fluids intersect in the device (Fig. 8.6b). These emulsions are exposed to UV (265 nm) at the device outlet thereby polymerizing the PDMS monomer shell, yielding elastomer microbubbles. Through careful changes to the middle phase flow rate from 1, 1.5, to 2.0 mL/h, we obtain three distinct shell thicknesses, as shown in Fig. 8.6c.

PDMS elastomers are advantageous being both chemically inert and mechanically stable up to 200°C, while also highly permeable to most gases. For applications such as enhanced oil recovery, a microbubble is forced through a confined geometry, its volume decreases, and the interior pressure increases; allowing gases to permeate the shell may relieve this stress. Therefore, we fabricate both impermeable and permeable microbubbles by choosing a continuous phase during fabrication of either 20wt% polyvinyl alcohol (PVA, \(~88\%\) hydrolyzed) or 10wt% polyethylene glycol (PEG) with sodium dodecyl sulfate as surfactant. Partially hydrolyzed PVA is used as a polymeric surfactant in microfluidic experiments as it provides not only interface stability but also a high shear stress due to its increased viscosity over dilute surfactant solutions \cite{179}. However, PVA is also an excellent film former \cite{180}; even after many washings
with water, a residual surface film is nearly always present [181, 182]. It is this surface film that inhibits the gas permeability of the PDMS shell. By contrast, a solution of PEG and SDS, increases viscosity and interface stability, respectively, but does not irreversibly adsorb to the interface; thus permitting gas transport through the PDMS shell.

### 8.2.2 Mechanical testing using a μN force compression apparatus

To evaluate the mechanical properties of these microbubbles, we use a parallel plate-plate compression apparatus constructed of two silicon wafers, an analytical
balance and a linear translation motor, as shown in the schematic in Fig. 8.7a. The microbubble is placed on a silicon wafer that is affixed to the plate of the analytical balance; a precision of 0.1mg enables measurement of forces below $10^{-6}$N. A silicon wafer affixed to the linear motor serves as the top plate. We program the linear motor to make predetermined displacement steps, applying a fixed strain to the microbubble while measuring the balance readout. To conduct a force-displacement measurement, the point of first contact between the microbubble and top plate is set as the zero-displacement. Due to the reflectivity of silicon, the reflection of the microbubble is seen on both the top and bottom plates, as shown in the second panel of Fig. 8.7b. The top plate is lowered to its first position, and the microbubble deforms; after adequate relaxation time, the compression cycle continues. At maximal compression (strain $\sim$70%), the decompression cycle begins. In a typical force versus displacement curve for the compression, such as the one plotted in Fig. 8.7c, we do not observe hysteresis. The slope of the loading curve is low ($\sim$0.5) up to a displacement of 60$\mu$m and increases to 1.7 until loading is complete, thereby indicating that less force is required to make the initial deformations. At more significant deformations, greater force is required, due to an increase in the internal pressure within the impermeable microbubble. By contrast, from the point of maximum displacement, the unloading curve begins with a high negative slope of -0.9 to 160$\mu$m and decreases to a lower slope of -0.6 until 60$\mu$m. Notwithstanding these differences in the shapes of the curves, the area under each curve remains the same, thereby indicating equivalent work is required for compression and decompression. These deformation experiments are repeated for permeable microbubbles.
We numerically investigate the deformation of the microbubbles by using the commercial finite element software Abaqus. 2D axisymmetric models are meshed with approximately 1500 4-node bilinear axisymmetric quadrilateral elements with reduced integration (element type CAX4R in Abaqus) and the accuracy of each mesh is ascertained through a mesh refinement study. The response of the microbubble is captured by using a nearly-incompressible Neo-Hookean model [183] (with Poisson’s ratio \( \nu = 0.49 \)), whose strain energy density is given by

\[
U = \frac{G_0}{2} (\bar{T}_1 - 3) + \frac{K_0}{2} (J - 1)
\]

where \( \bar{T}_1 = J^{-2/3} tr[\text{dev}(F^TF)] \), \( J = \det(F) \) and \( F \) is the deformation gradient. Moreover, \( G_0 \) and \( K_0 \) are the shear and bulk modulus in the undeformed configuration and they are obtained by fitting the response under uniaxial compression of the bulk materials, resulting in \( G_0^{imp} = 40 \text{kPa}, K_0^{imp} = 1987 \text{kPa} \) and \( G_0^p = 60 \text{kPa}, K_0^p = 2980 \text{kPa} \) for impermeable and permeable bubbles, respectively.

### 8.2.3 Finite element simulation

To accurately simulate the microbubble response, we account for the pressure on the shell that is exerted by the contained gas using the surface-based fluid cavity capability in Abaqus. Particularly for the permeable microbubbles, we assume that the gas in the core is in equilibrium with the surrounding environment and at atmospheric pressure. By contrast, for the impermeable microbubbles, we account for the fact that the gas inside the cavity may be at a higher pressure than the surrounding environment considering pressures ranging from 1 atm to 1.5 atm. The microbubble compression is simulated using the dynamic explicit solver and quasi-static condi-
tions are ensured by monitoring the kinetic energy and introducing a small damping factor. As in the experimental setup, in the simulation, two parallel rigid plates are used to compress each microbubble: the bottom plate is stationary and the top plate is displaced in the loading direction. No friction between the microbubbles and the plates is considered.

In Fig. 8.8, we show a comparison between the experimental and numerical results obtained from compression tests of both the permeable and impermeable microbubbles. As shown in the top panel, for the impermeable bubble, the maximum stresses occurs at the inner core of the microbubble shell as a result of the inside pressure. In particular, when the impermeable bubble is compressed to a strain of 30%, a maximum von Mises stress of 65 kPa is observed. Interestingly, the response of the permeable microbubble is more compliant, despite the fact that the shear modulus of the material is larger, $G^\text{Imp}_0 < G^P_0$. In fact, when the permeable microbubble is compressed to 28%, a maximum von Mises stress of 47 kPa is found, as shown in the bottom panel in Fig. 8.8. Moreover, the stresses are localized to the outer surface of the shell at the point of contact with the top and bottom plates. The difference in the stress magnitude and distribution highlight the importance of permeability in microbubble compression.

To validate our numerical results, we quantitatively compare our experimental force-strain curves with those of the simulations. As reported in Fig. 8.9, the comparison shows a very good agreement over a wide range of applied deformation. For the impermeable microbubble we find that the experiment has a best-fit with the numerical model at the highest pressure of 1.5 atm, thereby indicating, the PVA coating
Figure 8.8: A comparison of experimental and simulation results of impermeable and permeable microbubbles. In the top panel, an impermeable bubble with outer diameter $D_{\text{out}}=446 \mu m$ and inner diameter $D_{\text{in}}=365 \mu m$ is uniaxially compressed to a strain=$-0.30$. The corresponding stress distribution diagram shows a maximal von Mises stress of 0.065 MPa. In the bottom panel, a permeable bubble ($D_{\text{out}}=380 \mu m$ and $D_{\text{in}}=310 \mu m$) is compressed to a strain=$-0.28$ with a corresponding stress distribution diagram showing a maximal von Mises stresses of 0.047 MPa.
Figure 8.9: A comparison of force versus strain between experimental results and simulation for the impermeable (a) and permeable (b) microbubbles. Note: the impermeable bubble is best fit by a high internal pressure, 1.5 atm, and the permeable bubble shows hysteresis upon unloading, $\epsilon_{\text{unloading}}=0.2$.

serves as a barrier to the gas contained within the cavity of the microbubble. Moreover, the exponential shape of the curve for the impermeable microbubble further confirms the influence of the impermeable shell on mechanical properties as the curve indicates that greater force is required to deform the microbubble shell after a critical strain value of 20%, as shown in Fig. 8.9a. By contrast, for the permeable bubble, the shape of the force-strain curve is linear; the permeable bubble acts as a simple linear spring with no pressure increase.

We validate the mechanical resilience of these well-characterized microbubbles by passing them through constrictions that simulate the porous space of the end-use application: porous rock in oil reservoirs. To conduct this simple test, we pull a glass capillary to have a single smooth constriction into which one permeable microbubble is loaded. We connect the entrance of the capillary to a pressure source equipped...
Figure 8.10: Stages of microbubble transit through a glass constriction. The position of the microbubble in a and b is at equilibrium with the applied pressure. The applied pressures are (a) = 0.5psi, (b) = 4.5psi, and (c) = 6.1psi.

with a pressure transducer; the exit is open to atmospheric pressure. Initially, at low pressure, the microbubble starts before the constriction, as shown in Fig.8.10a. As the pressure increases, the microbubble is forced into the constriction and deforms to the size of the constriction, as shown in Fig.8.10b. As the microbubble exits the constriction, it begins to recover its original shape and flows out the exit of the capillary, as shown in Fig.8.10c. This simple test demonstrates elastomer microbubble resilience in response to applied pressure as it passes through a constriction.

8.2.4 Section summary

In summary, we have used microfluidics to prepare PDMS elastomer microbubbles with controllable shell dimensions and permeability by varying the shell-coating. We
directly measured their mechanical properties through the use of a \( \mu \text{N}-\)scale parallel plate compression test, and used finite element to interpret these experimental results. The ability to use numerical models expands the possibilities of designing microfluidic microbubbles with predictable mechanical properties.

### 8.2.5 Experimental for this section

All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. The external continuous phase consisted of either 10mM sodium dodecyl sulfate (SDS) and 10wt\% polyethylene glycol (Mn\( \sim \)20,000g/mol) or 20wt\% polyvinyl alcohol (Mw\( \sim \)13,000-23,000g/mol, 87-89% hydrolyzed) in water which were bubbled with nitrogen for 15 minutes prior to use in the microfluidic device. The shell fluid is composed of a UV curable PDMS formulation [184]: 1wt\% of photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, was dissolved into methacrylate modified PDMS prepolymer, RMS-033 (Gelest). This mixture was bubbled with nitrogen for 15 minutes prior to use in the microfluidic device. The inner dispersed phase was a nitrogen source used at a fixed pressure of 15psi.

The glass capillary microfluidic device was fabricated according to published methods [178]. Square glass capillaries were purchased from Atlantic International Technologies. Round glass capillaries were purchased from World Precision Instruments and tapered using a Sutter P-97 capillary puller. For the constriction experiments, a 1mm inner diameter capillary was pulled but not to the point of pinch-off. The parallel plate-plate compression apparatus was constructed using a Mettler Toledo AT261 analytical balance recording the mass every second. The compression was
controlled using a Newport Controller ESP300 operating a linear translation stage, Newport LTA-HL. To guarantee that both silicon wafers were parallel, the unpolished side of one silicon wafer was affixed to the balance pan using epoxy. The polished sides of the two wafers were then brought into physical contact. The translation stage was lowered and epoxy was used to affix the top silicon wafer to the stage; once cured the stage was raised and a single microbubble loaded between the plates. A compression test consisted of a single displacement step with a 15 minute relaxation pause between steps to allow stresses to dissipate within both the permeable and impermeable microbubbles.

### 8.3 Soft PDMS bottlebrush elastomers

PDMS elastomers, or silicone rubbers, are widely used in both industry and research, largely because they are optically clear, inert, non-flammable, and in general, non-toxic and easy to process ([185, 186, 187, 188, 189, 190, 191, 192, 193, 194]). A typical PDMS elastomer is made of covalently crosslinked entangled linear polymers in a melt. However, it cannot have a shear modulus lower than 200 kPa due to entanglements which act as effective crosslinks; adding covalent crosslinks to an entangled melt is required to form a network, but only increases the network modulus [195, 196, 197]. To achieve a low modulus, one may crosslink PDMS molecules in a polymer liquid to form a gel. Compared to an elastomer without solvents, a gel is of lower density of crosslinks and thus softer, due to the extra volume occupied by the polymer liquid. While this method is simple, and commonly used for commercial silicone products, the liquid not only makes the gel adhesive, but also leaches out.
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An alternative strategy is to first form a gel by crosslinking linear polymers in a solution of low concentration, such that the polymers are not entangled. Based on such an unentangled gel, additional polymers are then grafted from the strands between crosslinks [198, 199, 200]. After removing the solvent molecules, one obtains a ‘dry’, unentangled network; it can be soft, as the grafted polymers decrease the density of crosslinks, by effectively increasing the molecular weight of network strands, and thus lower the modulus. Unfortunately, however, this multi-step approach is often severely limited by its complex synthesis, which makes it difficult to obtain a final product of desired stiffness; in addition, this approach has not yet been explored for fabrication of PDMS elastomers. It remains a challenge to design and fabricate soft, solvent-free PDMS elastomers with controllable stiffness.

In this section, we develop a one-step process to fabricate soft PDMS elastomers by crosslinking brushlike rather than linear polymers. The fabrication process is as easy as that for commercial silicone elastomer kits. Moreover, the soft PDMS elastomers are solvent-free, and have precisely controllable moduli ranging from 1 to 100 kPa, beyond the lower limit of typical PDMS elastomers. Remarkably, the moduli are in excellent agreement with theoretical predictions on the basis of classical rubber elasticity: The modulus is linearly proportional to the density of crosslinking chains. We show that the soft PDMS elastomers are qualitatively different from commercial silicone products of similar stiffness in their significantly lower amount of uncrosslinked, free molecules and lower adhesion.
Figure 8.11: Molecular design of soft elastomers. (A) Schematic view of a conventional elastomer formed by crosslinking linear polymers: Red circles denote chemical crosslinks, and topologically trapped lines denote entanglements. (B) Schematic view of a soft elastomer fabricated by crosslinking brushlike polymers: A multifunctional linear polymer chain acts as backbone (black); it is grafted by many side chains (blue), which are relatively short, mono-functional linear polymers carrying one reactive site, and crosslinking chains (red), which are di-functional linear polymers. (C) Three types of precursor reactive linear PDMS polymers form the structure described by (B) through hydrosilylation reaction with the aid platinum catalyst at 80°C.
8.3.1 Soft elastomer design

To fabricate a soft elastomer, the entanglements must be eliminated. To this end, the entanglement molecular weight must be increased significantly; this is impossible for linear polymers in a melt, as they start to entangle at relatively low molecular weight [195, 196, 197]. Unlike a linear polymer, a bottlebrush molecule has many relatively short linear polymers chemically attached to a long linear backbone molecule [201]. This brushlike molecule can be considered a linear yet fat polymer, but with the entanglement molecular weight orders of magnitude higher than that of linear polymers. For instance, for linear PDMS polymers the entanglement molecular weight is \( \sim 10^4 \text{ g/mol} \) [202]; by contrast, for brushlike PDMS polymers it can easily be \( > 10^7 \) g/mol. Therefore, using bottlebrush polymers enables elimination of entanglements unless the molecular weight of brushlike molecules is extremely high, as illustrated in Fig. 8.11a,b.

However, this “architecture-driven disentanglement” strategy for fabrication of elastomers involves synthesizing the brushlike polymers and crosslinking them, which typically requires multiple steps. Therefore, the key to developing a one-step method for fabrication of soft elastomers is to design the chemistry so that the reactions for forming brushlike molecules and for crosslinking proceed concurrently under the same condition.

To demonstrate this concept for PDMS systems, we use the well-established hydrosilylation of PDMS [203], which proceeds by the addition of Si-H bonds to unsaturated bonds like vinyl groups, as shown in Fig. 8.11c. From commercially available products, we identify a reactive PDMS polymer that is suitable for the back-
bone (BB) of brushlike molecules, vinylethylsiloxane-dimethylsiloxane terminated by trimethylsiloxy with molecular weight $\langle M_w \rangle = 50,000$ g/mole, Fig. 8.11C). This linear PDMS is copolymer that carries many vinyl groups (reactive sites B), about 300 per molecule, and an equal number of regular dimethylsiloxane units. These regular units are important as they promote the miscibility of vinyl functionalized PDMS with other reactive PDMS polymers [204]. Similarly, a commercially available PDMS polymer with $\langle M_w \rangle = 4,750$ g/mol, carrying one hydride group (reactive site A) at one of its two ends, serves as a side chain (SC) by grafting to the backbone polymer via a hydrosilylation reaction between hydride and vinyl groups. The A-B reaction results in the formation of brushlike molecules. To crosslink brushlike molecules, we use dihydride terminated PDMS polymer that has a hydride group (reactive site A) on both ends, as crosslinking chains (CLs) to bridge backbone of the brushlike molecules. The crosslinking chain has molecular weight of 17,200 g/mole, larger than twice the side chain that defines the geometric separation between backbone molecules. The reactions for forming brushlike polymers and crosslinking them are both hydrosilylation, as shown in Fig. 8.11c; this feature should enable a one-step synthesis of soft PDMS elastomers with structure illustrated by Fig. 8.11b.

Indeed, the fabrication of soft PDMS elastomers is as simple as that of commercial silicone kits. We mix the three types of precursor linear PDMS polymers with prescribed ratios, add platinum as catalyst, and elevate the temperature to 80°C to accelerate polymerization, Table 8.1. The complete polymerization requires all the reactive groups A carried by side chains and crosslinking chains successfully reacting with groups B on backbone molecules. This process will become more difficult
Table 8.1: Recipe for fabrication of soft PDMS elastomers presented as molar ratio of each polymer component. The mixture is polymerized with the addition of Karstedt’s Catalyst at concentration of 5 µl/g. Equilibrium shear storage modulus is taken as the measured value at oscillatory frequency of 0.01Hz, temperature of 20°C, and fixed strain of 0.5%.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Backbone (50kg/mol)</th>
<th>Side Chain (4.7kg/mol)</th>
<th>Crosslinking Chain (17.2kg/mol)</th>
<th>Extension Chain (10kg/mol)</th>
<th>Shear Modulus (Pa)</th>
<th>Solid Fraction (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE60</td>
<td>1</td>
<td>30</td>
<td>60</td>
<td>0</td>
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<td>93.8</td>
</tr>
<tr>
<td>SE30</td>
<td>1</td>
<td>90</td>
<td>30</td>
<td>0</td>
<td>84,100</td>
<td>–</td>
</tr>
<tr>
<td>SE10</td>
<td>1</td>
<td>130</td>
<td>10</td>
<td>0</td>
<td>34,700</td>
<td>85.6</td>
</tr>
<tr>
<td>SE5</td>
<td>1</td>
<td>140</td>
<td>5</td>
<td>0</td>
<td>20,400</td>
<td>–</td>
</tr>
<tr>
<td>SE1</td>
<td>1</td>
<td>148</td>
<td>1</td>
<td>0</td>
<td>11,800</td>
<td>–</td>
</tr>
<tr>
<td>SE0</td>
<td>1</td>
<td>150</td>
<td>0</td>
<td>0</td>
<td>8,940</td>
<td>78.0</td>
</tr>
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<td>150</td>
<td>0</td>
<td>150</td>
<td>7,430</td>
<td>76.2</td>
</tr>
</tbody>
</table>

when approaching to the end of polymerization, probably due to increase in steric hindrance when more reactive sites B on the backbone are occupied. We therefore use a recipe that ensures an excess amount of reactive sites B compared to A, even if the system is fully polymerized, by keeping the molar ratio between reactive sites A and B at 1:2. To quantify the time required for complete polymerization, we monitor the viscoelastic properties of the mixture in situ using rheometer at oscillatory shear frequency of 1Hz and constant strain of 0.5%. We observe that shear storage modulus increases significantly within the first a few hours, exceeding the shear loss modulus, and reaches a stable value after about 40 hours, as shown in Fig. 8.12a.
Figure 8.12: Rheological properties. (a) Dependence of viscoelastic properties of representative soft PDMS elastomers on curing time measured at 80°C, 1 Hz, and a fixed strain of 0.5%. (b) Frequency dependence of the storage (red symbols, G') and loss (blue symbols, G'') moduli of representative soft elastomers measured at 20°C at a fixed strain of 0.5%. Different symbols show soft elastomers corresponding to different number of crosslinking chains per brushlike molecule: Triangle, SE60, square, SE30, and circle, SE0. Detail recipe of each sample is listed in Table 8.1. (c) Dependence of equilibrium shear modulus of soft elastomers on density of crosslinking chains. The equilibrium moduli are taken as the values measured at frequency of 0.01 Hz, temperature of 20°C, and strain of 0.5%. The density of crosslinking chains is presented by \( (n_{cl}^{eff} - 1)/M \), see text. The green circle represents sample SEL. Solid line represents the best fit using equation (1): \( G = (2530 \text{ Pa})/(10^6 \text{g/mol}) \left( (n_{cl}^{eff} - 1)/M \right) \). Insert: The density of crosslinking chains is calculated based on the assumption that all crosslinking chains successfully bridge neighboring brushlike molecules and there are no “impurities” in side chains. Solid line represents the best fit to the data: \( G = (2530 \text{ Pa})/(10^6 \text{g/mol}) \left[ (n_{cl} - 1)/M \right] + 9370 \text{ Pa} \).
8.3.2 Soft elastomer rheology

The storage moduli, $G'$, of polymerized samples are almost independent of oscillatory shear frequency; they vary less than 10% with frequency ranging from four orders of magnitude $10^{-2}$ to $10^2$ Hz, as shown in Figs. 8.12. Therefore, it is reasonable to take the value of $G'$ at the lowest frequency 0.01Hz as the equilibrium modulus, $G$, of the network. Remarkably, the value of $G$ for all elastomers formed by crosslinking brushlike PDMS is lower than the plateau modulus $2 \times 10^5$ Pa of entangled linear PDMS melts.

The fact that we can achieve such low elastic moduli is due to the unique role of relatively short side chains. The side chains have and $\langle M_w \rangle = 4,750$ g/mol, below the entanglement threshold 12,000 g/mol, and thus are not entangled. Importantly, these short side chains act as large solvent species for the longer backbone molecules and crosslinking chains; this promotes the chemical reaction yet avoids formation of entanglements before polymerization, see Section 8.3.6. After reaction, the short side chains become chemically attached solvent species by grafting to the long linear backbone molecules; they serve as a part of the network, but do not directly contribute to the network elasticity.

To quantitatively understand the elasticity of soft elastomers, we apply the classical estimate for elasticity of a rubber without entanglements [205]. The equilibrium modulus $G$ of an affine, unentangled network is proportional to the density of elastically effective network strands; this affine network model assumes all crosslinks are attached to a fixed background and all network strands deform in the same manner under macroscopic deformation. However, the crosslinks, in reality, can fluctuate; as
a result, the shear modulus is lower than that of an affine network. Indeed, it can be described by the phantom network model: \( G = kT(\nu - \mu) \), where \( k \) is Boltzmann constant, \( T \) is absolute temperature, \( \nu \) and \( \mu \) are the densities of elastically effective network strands and crosslinks respectively \([195, 196]\).

In the soft PDMS elastomers, however, not all polymer strands and crosslinks are elastically effective. In fact, the dangling side chains and the corresponding dangling crosslinks are not elastically effective, as they cannot sustain stress. Therefore, the elastically effective network strands and crosslinks are solely due to the reaction between backbone polymers and crosslinking chains. A crosslinking chain can react with a backbone polymer by grafting one of its two ends to it, leaving the other end unreacted. It can also react with the same backbone polymer by attaching both the two ends to it and thus form a loop. For these two cases, the reaction between crosslinking chain and backbone polymer does not contribute elastically effective crosslinks nor network strands. By contrast, a fully reacted, bridging crosslinking chain adds two elastically effective crosslinks; in addition, by dividing the backbone polymers into two more sections, it contributes three additional elastically effective network strands, including the crosslinking chain itself and two strands along backbone polymers. However, the first elastically effective crosslink on each backbone polymer is not by itself elastically effective and requires additional crosslinking strands. Thus, for a network with an average \( n_{cl} \) fully reacted, bridging crosslinking chains per brushlike molecule, there are \( 3n_{cl} - 1 \) network strands and \( 2n_{cl} \) crosslinks that are elastically effective per brushlike molecule. The modulus of such a network is \( G = kT(n_{cl} - 1)\rho/M \), in which \( \rho = 0.97 \text{ g/cm}^3 \) is the density of PDMS \([206]\), and \( M \) is the mass of the brushlike...
molecule that includes backbone polymer, side chain, and crosslinking chain. This expression predicts that the moduli of the unentangled elastomer can be tuned by varying 1) either the number \( n_{cl} \) of crosslinking chains per brushlike molecule or 2) the molecular weight \( M \) of the brushlike molecule.

To test this hypothesis, we fix the molar ratio between reactive sites A and B at 1:2, but vary the molar ratio between backbone polymers and crosslinking chains; each di-functional crosslinking chain is equivalent to two mono-functional side chains in terms of the number of reactive sites, as listed in Table 8.1. This enables almost unchanged molecular weight, as the molecular weight of crosslinking chain is about twice of a side chain, but different number of crosslinking chains per brushlike molecule. We find that the modulus of soft elastomer is linearly proportional to the number of crosslinking chains per brushlike molecule, as shown by the insert in Fig. 8.12c. The slope of this linear dependence, 2530±210 Pa, is in good agreement with the predicted value \( kT\rho/(10^6 \text{ g/mol}) = 2400 \text{ Pa} \), corresponding to the modulus for one crosslinking chain per PDMS brushlike molecule of molecular weight \( 10^6 \text{ g/mol} \). However, the modulus of soft elastomers does not vanish when there is on average one crosslinking chain per brush molecule, which seems to contradict with prediction [185]. Indeed, this discrepancy suggests that there might be “impurities”, crosslinking chains, in the commercially available side chains. To estimate the fraction of “impurities”, we measure the modulus \( G \) of sample SE0 that contains only backbone polymers and side chains with molar ratio 1:150. The modulus of SE0 is \( G=8940 \text{ Pa} \), which gives the fraction of “impurities” in side chains: \( f_{ip} = [GM/(pkT) + 1]/n_{sc} = 2.56x10^{-2} \), where \( n_{sc}=150 \) is the number of side chains per brushlike molecule. Taking into account
the “impurities” in side chains, we calculate the effective number of fully reacted, bridging crosslinking chains per brushlike molecule using $n_{cl}^{eff} = n_{cl} + n_{sc}f_{ip}$, and re-plot the moduli of soft elastomers as a function of $(n_{cl}^{eff} - 1)/M$. They are in perfect agreement with the classical phantom network prediction by the above equation, $G = (2530 \pm 210) \text{ Pa (10}^6 \text{ g/mol) (} n_{cl}^{eff} - 1)/M$, as shown by the red symbols and solid line in Fig. 8.12c.

In addition to varying the number of crosslinking chains per brushlike molecule, we demonstrate the ability to tune the modulus of soft elastomers by controlling molecular weight of the brushlike molecule. On the basis of sample SE0 that contains only backbone molecules and side chains, we introduce another type of commercially available linear polymer, monovinyl-monohydride terminated PDMS. It has molecular weight of 10,000 g/mol and two ends functionalized differently, one carrying reactive site A, while the other carrying reactive site B. These polymers can either react with short, mono-functional side chains to form longer side chains or directly graft to backbone molecules. Thus, they effectively act as extension chains (EXTs), increasing the molecular weight of the brushlike molecule, but without changing the number of grafting sites on the backbone molecule. Therefore, the addition of extension chains should result in decrease of network modulus. Indeed, the modulus of sample SEL, in which the molar ratio of BB: SC: EXT = 1:150:150, is 7430 Pa, lower than 8940 Pa of sample SE0 with BB: SC = 1:150 (Table 8.1). This value is in good agreement with the prediction from the above equation, as shown by the green point in Fig. 8.12c, by taking into account the “impurities” crosslinking chains in the commercially available extension chains. This agreement demonstrates the concept that the modulus of soft
elastomers can be tuned by changing the molecular weight of brushlike molecules.

To quantify the soluble fraction, we perform Soxhlet extraction for 60 hours using acetone/n-hexane (50:50) to remove the unreacted polymers, and measure the remaining mass after drying, see section experimental section. The ratio of remaining to the initial mass is termed solid fraction. For soft PDMS elastomers, we find that the solid fraction is about 94% (wt/wt) for G~10^5 Pa and decreases slightly to 86% for G~40 kPa, yet still remarkable, ~76%, when the elastomers become very soft, with the modulus on the order of kPa (Table 8.1). By contrast, for commercially available Sylgard PDMS elastomers, the solid fraction is only ~50% when G~40 kPa; moreover, it decreases dramatically when becoming softer. For instance, the solid fraction is <2% for G~1000 Pa. Therefore, compared to the Sylgard PDMS products of similar moduli, the soft PDMS elastomers have superior properties in remarkably less soluble fraction, though it increases slightly when becoming softer.

8.3.3 Soft elastomer adhesion

The uniqueness of soft PDMS elastomers can be further highlighted by a parameter, tackiness, an important measure when involving direct contact of PDMS elastomers to tissue, such as ingredients for cosmetics and skin care [186, 207]. To characterize the tackiness of soft PDMS elastomers, we perform JohnsonKendall-Roberts (JKR)-type measurements by bringing a spherical steel ball and a flat sheet of soft elastomers into contact, as illustrated in Fig. 8.13a [207]. The adhesion force, acting across the ball-elastomer interface, tends to deform the elastomer and thus to increase the area of their contact. Since this deformation is opposed by the elastic
Figure 8.13: Adhesion. (a) Schematic of adhesion test by retracting a steel ball with diameter 3.55mm from elastomer films with controlled velocity $\nu$ after indentation. The adhesion force between the ball and the film is measured by a microbalance underneath the film. (b) Representative images showing the contact between the different elastomers and ball at zero displacement $d - d_0 = 0$ for the ball is retracted at $1 \mu m/s$. (c) Representative curves for retracting the ball at $1 \mu m/s$ from elastomer films after indentation. The shadowed area represents the adhesion energy required to separate the ball from the elastomer films. (d) Dependence of adhesion energy on ball-film separation rate for soft elastomers (circles and squares) and commercially available elastomers (triangles). Data are shown as mean ± SD with the number of samples $n=3$. 

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restoring force, its magnitude is higher for elastomers of higher adhesion, providing the same elastic modulus. For soft elastomer SE30 and Sylgard PDMS 1:50 that are of similar modulus $G \sim 40$ kPa, we find that the deformation of latter one is obviously larger, as shown by the optical images in Fig. 8.13. Moreover, the deformation of a commercial silicone CY 52-276, with modulus on the order of kPa, is significantly larger compared to soft elastomer SE0 of similar stiffness, as shown in 8.13b. The relatively small deformation of soft PDMS elastomers suggests they are less adhesive compared to commercial silicone products of similar stiffness.

To quantify the adhesive properties, we indent the steel ball into a flat elastomer sample, retract it with controlled velocity, and measure the retracting force, as illustrated in Fig. 8.13a. The force is initially positive, due to the elastic restoration of the compressed elastomer. As the ball retracts, the elastomer becomes less compressed and thus elastic restoration force decreases. The elastic restoration is balanced by the adhesion at a certain displacement. As displacement increases beyond this point, the adhesion dominates and thus the force becomes negative till the separation of ball from the elastomer, at which the ball is typically higher than the surface of the undeformed PDMS slab. This adhesion-dominated window is presented by the shadowed area in the force profile, as shown in Fig. 8.13c. The area represents the work, termed adhesion energy, $E_{adh}(v)$, required to separate the ball from the PDMS slab at rate $v$. Consistent with tackiness apparent in Fig. 8.13b, we find that $E_{adh}$ for soft PDMS elastomers at separation rate $10\mu m/s$ is about one order of magnitude lower than that for the Sylgard product of similar modulus. In addition, compared to another commercial silicone product, CY 52-276, the adhesion energy for soft PDMS elastomers,
E_{adh}(v=10\mu m/s), is lower by more than two orders of magnitude, as shown by the symbols on the right of Fig. 8.13d. Interestingly, E_{adh} for soft PDMS elastomers is almost independent of separation rate; by contrast, the commercial silicone products have adhesion energy increasing with separation rate, as shown in Fig. 8.13d. The lower adhesion energy of soft PDMS elastomers can be qualitatively understood on the basis of energy dissipation, which accounts for the excess amount of energy to separate two surfaces in addition to surface tension. The amount of dissipated energy at a certain separation rate is lower for elastomers materials with less soluble fraction and thus lower viscous modulus. In addition, the dissipated energy for viscoelastic polymers is typically proportional to the separation rate with a power between 0.4 and 1, which is consistent with our results for commercial silicone products, as shown in Fig. 8.13d. However, complete understanding of the dependence of adhesion energy on separation rate remains a mystery and will be subjected to future study. Nevertheless, our results demonstrate that the soft PDMS elastomers are different from commercial silicone products of similar stiffness in their significantly less tackiness.

The commercial silicone products are biocompatible in general; however, this is unclear for soft PDMS elastomers. Therefore, we perform a biocompatibility test by cultivating MDCK epithelial and NIH/3T3 fibroblast cells on substrates made by the soft PDMS elastomers of different moduli and monitoring their growth. Both the two cell types spread on the substrates after 24 hours and confluent within about 72 hours, as shown by Fig. 8.14. However, a clear proliferation increase is seen on stiffer substrates while spread area appears constant; spread area and proliferation rate are thought to be directly correlated, this disconnect is interesting. Further understand-
Figure 8.14: Cell growth. Fluorescence and phase contrast images showing the proliferation of MDCK epithelial (a) and NIH/3T3 fibroblast (b) cells at 24, 48, and 72 hours on substrates formed by soft PDMS elastomers with storage moduli of 7 kPa, 20 kPa, and 80 kPa. Images are 750μm x 750μm.

...ing cellular responses, such as spreading area, volume, and differentiation[208], to substrates made of soft PDMS elastomers are beyond the scope of this chapter and will be subjects of further explorations.

8.3.4 Section summary

We have developed a one-step synthesis of soft PDMS elastomers by crosslinking brushlike polymers; they have elastic modulus beyond the lower limit of typical PDMS elastomers fabricated by crosslinking linear polymers. Compared to hydrogels [209], the soft PDMS elastomers described here do not reach a low limit <1000 Pa; however, in principle, even lower modulus, <100 Pa, can be achieved by using long backbone and side chain molecules without impurities. Unlike commercial soft silicone products, soft PDMS elastomers have remarkably less soluble fraction and significantly less...
tackiness. In addition, the simplicity of the synthesis, the commercially available raw ingredients, and additional flexibility of choosing backbone/side chain/crosslinking chain ratio provide a useful tool with which to precisely tune the mechanical properties of soft PDMS elastomers. This versatility, together with the biocompatibility of soft PDMS elastomers, is not only an asset for industrial development of critical ingredients for personal care products as well as soft materials for biomedical research and engineering, but also offers a model system for understanding the challenging physics of unusual elasticity, dynamics and relaxations of soft elastomers. Finally, the one-step fabrication method proposed here is not restricted to PDMS; it should be general and will enable exploration of soft elastomers made of other polymers.

8.3.5 Experimental for this section

All chemicals are purchased from Sigma-Aldrich (St. Louis, MO) unless otherwise noted. All reactive PDMS polymers are purchased from Gelest Inc. (Philadelphia, PA) and used as received. Backbone: vinylmethyldimethyldimethylsiloxane copolymer, trimethylsiloxy terminated, \(~300\) vinyl groups per molecule, \(\langle M_w \rangle \sim 50,000\) g/mol (VDT-5035). Side chain: mono-hydride terminated polydimethylsiloxane, MW\(~4,750\) g/mol (MCR-H21). Crosslinking chain: hydride-terminated polydimethylsiloxane, \(\langle M_w \rangle \sim 17,200\) g/mol (DMS-H25). Extension chain: \(\alpha\)-monovinyl-\(\Omega\)-monohydride terminated polydimethylsiloxane, \(\langle M_w \rangle \sim 10,000\) g/mol (DMS-HV22).

The PDMS linear polymers are mixed at a predetermined mass ratio to achieve different density of crosslinking chains. Catalyst, 2% platinum in xylene, so called Karstedt’s catalyst, is added at the concentration of 5 \(\mu\)l/g. The mixture is cured at
80°C for 40 hours to reach a steady shear storage modulus. Rheological experiments are carried out on a strain controlled rheometer (MCR501, Anton Paar) with 50 mm plate-plate geometry at a gap of 750 µm. Frequency sweeps are performed from $10^2$ to $10^{-3}$ Hz at 0.5% strain at temperatures 80°C, 20°C, and −20°C. Changes in normal force due to a gap contraction with temperature are alleviated by adjusting the gap height.

To quantify the solid fraction of soft elastomers, we use standard Soxhlet method to remove unreacted molecules in the polymerized PDMS-catalyst mixture. We perform the extraction in acetone/n-hexane (50:50) for 60hrs, and then dry the swollen PDMS gel in a vacuum oven at 80°C for 24hrs; after that the mass of PDMS does not decrease. The mass of the insoluble gel fraction is divided by the total mass before extraction and the values are listed in

To prepare substrates for mammalian cell growth, we place 150 µl of the PDMS-catalyst mixture in each well of a 24-well plate and cure at the same condition above. We then add 1 ml of 1M KOH to each well for 1hr to gently treat the surface of soft PDMS elastomer instead of using plasma; plasma oxidation can crosslink the surface of PDMS, yielding a stiffer substrate [210]. The surface is silanized by adding 500µl of 1% (v/v) glycidyl propyl trimethoxysilane (Gelest Inc.) in ethanol, and 500µl 1% (v/v) ammonium solution in water sequentially to each well. After 10 minutes, the surface is cleaned using ethanol, and then 1x phosphate buffered saline (PBS), twice. We add 500 µl of 0.1 mg/ml collagen (Type 1) to each well and store the plate at 4°C to prevent collagen polymerization but allow the collagen to react to the glycidyl group on the silanized PDMS surface. The collagen coated surfaces are washed with
1x PBS twice, then culture media: 10% fetal bovine serum (FBS) and 1% pen-strep in Dulbecco’s modified eagle medium (DMEM). 1 ml of culture media is placed in each well and warmed to 37°C. Two cell types are used: Madin-Darby canine kidney (MDCK) epithelial cells (NBL-2, ATCC CCL-34TM), which have been stably transfected with plasmid pCMV LifeActTagGFP2 (Ibidi), and NIH/3T3 fibroblasts (ATCC CRL-1658TM). We place trypsinized MDCK epithelial and NIH/3T3 fibroblast cells on the collagen functionalized substrates at an initial concentration of \( \sim 20 \) cells/mm\(^2\). We use fluorescence microscopy to image the fluorescent actin of MDCKs and phase contrast microscopy to image NIH/3T3s. Cell growth is monitored over 72 hours at the same location of the surface of substrate; culture media is not exchanged.

### 8.3.6 Bottlebrush theory

Consider a molecule with backbone of \( N_{bb} \) monomers and side chain of length of \( N_{sc} \) monomers. The side chains are densely grafted to the backbone polymer, forming a bottlebrush-like molecule, and occupy the cylindrical space surrounding the backbone polymer. The cross section of the cylindrical space is about the size \( R_{sc} \) of a side chain; it increases as the distance \( d \) along the backbone between two neighboring grafting sites decreases. However, the volume occupied by a side chain \( v_{sc} \) is constant; it is proportional to the number of monomers per side chain: \( v_{sc} = N_{sc} v_0 \), in which \( v_0 \) is the volume of a monomer. This side chain fills the volume \( R_{sc}^2 d \), which is the space available for it within the cylindrical volume of the bottle brush. Therefore, the size of a side chain is,
suggesting the cross section of the bottle-like brush molecule increases with the linear grafting density $1/d$.

The brushlike molecule may be considered a “fat” linear polymer, with effective monomer size, $b_{eff}$, about the cross section of size $R_{sc}$ of the brushlike molecule. An effective monomer contains $n_{sc} = R_{sc}/d$ side chains. Therefore, the total number of Kuhn monomers in an effective monomer is $N_{eff} = n_{sc}N_{sc} + R_{sc}/b$, in which $b$ is the spacing between backbone monomers along its contour and $R_{sc}/b$ counts for the number of Kuhn monomers of a section of stretched backbone polymer with size $R_{sc}$.

From eq. 8.1, we now equate the number of Kuhn monomers per effective monomer:

$$N_{eff} = \frac{N_{sc}R_{sc}}{d} + \frac{R_{sc}}{b} \approx N_{sc}^{3/2}v_0^{1/2}$$ (8.2)

The increase in size of an effective monomer compared to a Kuhn monomer suggests that the “fat” linear polymer becomes relatively stiffer, and thus easier to entangle. To estimate the entanglement molecular weight for the fat, brushlike polymer, we use the Kavassalis and Noolandi conjecture: The number of entanglement strands in the volume pervaded by an entanglement strand is about a constant value, $P$ with $P \approx \left[ b_{eff}(n_e)_{1/2}^3 / (b_{eff}^3 n_e) \right]$, in which $n_e$ is the number of effective monomers per entanglement strand, $[b_{eff}(n_e)_{1/2}]^3$ represents the volume pervaded by an entanglement strand of size $b_{eff}(n_e)^{1/2}$, and $b_{eff}^3 n_e$ corresponds to the volume of an entanglement strand. Therefore, the number of effective monomers per entanglement strand is: $n_e \approx P^2$. From eq. 8.2, the number of Kuhn monomers per effective monomer, the
number of Kuhn monomers per entanglement strand the “fat”, and the bottlebrush-like molecule is,

\[ N_e \approx n_e N_{eff} \approx P^2 N_{sc}^{3/2} v_0^{1/2} \frac{d^3}{2} \] (8.3)

The mass of a Kuhn monomer for PDMS is \( M_0 = 381 \text{ g/mol} \) (13). Thus, the number of Kuhn monomers per side chain of the molecular weight 4,750 g/mol utilized in this work is \( N_{sc} \approx 13 \). The backbone polymer is a copolymer of molecular weight 50,000 g/mol that contains \( \sim 600 \) chemical units. However, only half of the backbone polymer is reactive vinyl-monomer; thus, there are about 300 reactive vinyl groups for the block of backbone polymer. Only half of them are grafted by side chains. Therefore, the distance \( d \) between two neighboring grafting sites is about the length of two chemical monomers. The length \( l \) of a chemical monomer for PDMS (Si-O) bond is \( 1.64 \times 10^{-1} \text{ nm} \), which gives \( d = 2l = 3.28 \times 10^{-1} \text{ nm} \). The volume of a PDMS Kuhn monomer is \( v_0 = 6.50 \times 10^{-1} \text{ nm}^3 \) [195, 202]. For a typical value of \( P=20 \), the number of PDMS Kuhn monomers per entanglement strand of a ”fat” brushlike molecule is: 

\[ N_e \approx 20^2 \cdot 13^{3/2} \frac{6.50 \times 10^{-1} \text{ nm}^3}{3.28 \times 10^{-1} \text{ nm}^3}^{1/2} \approx 8.0 \times 10^5 \]. Thus, the entanglement molecular weight of the brushlike molecule is,

\[ M_e \approx N_e M_0 \approx 3.0 \times 10^7 \text{ g/mol} \] (8.4)

which is more than one order of magnitude larger than the molecular weight of the bottle brush molecule, \( \sim 10^6 \text{ g/mol} \), in the process of fabrication of the soft PDMS elastomers. Importantly, the entanglement molecular weight of the brushlike molecule suggests the lower limit of the modulus for soft elastomers; the modulus
can reach $G = kT \rho / M_e \sim 100 Pa$ by using longer backbone polymers. In addition, increasing the molecular weight of side chain by three times will result in even lower modulus, $3^{-3/2} \cdot 100 Pa \sim 10 Pa$, if the “impurities”, di-functional crosslinking chains, in mono-functional side chains can be removed.

As their molecular weight increases, the polymers overlap more, with more chains in the volume pervaded by one polymer. Polymers start to entangle with each other above a certain overlapping value. This crossover overlap parameter, $P_{20}$, is almost the same for polymers. Therefore, the entanglement molecular weight, $M_e \sim M_0 P^2$, varies slightly, within less than order of magnitude, as the molecular weight of a Kuhn monomer, $M_0$, varies little unless its chemical structure is modified [195]. To overcome this limitation, we change the chemical structure by using bottlebrush polymers rather than linear polymers, as illustrated in Fig. 8.11a,b. Unlike a linear polymer, a bottlebrush molecule has many relatively short linear polymers chemically attached to a long linear backbone molecule [201]. However, the brushlike molecule can still be considered a linear yet “fat” polymer, with the effective monomer size about its cross section size. This size increases with the degree of polymerization, $N_{sc}$, of grafted side chains and their grafting density, reciprocal of the space, $d$, between two neighboring anchoring points along the backbone. This gives the entanglement molecular weight of brushlike polymers: $M_{eb} \approx M_e N_{sc}^{3/2} (v_0 / d^3)^{1/2}$, where $v_0$ is the volume of a Kuhn monomer. Depending on the side chain length and grafting density, $M_{eb}$ can be orders of magnitude of higher compared to $M_e$.

The long, linear backbone polymer has molecular weight of 50,000 g/mol, above the entanglement molecular weight $M_e = 12,000 g/mol$ of linear PDMS polymers.
in melts [195]. Therefore, the backbone polymers may form entanglements before polymerization, though they are diluted by relatively short, unentangled side chains. These short side chains act as a θ-solvent for the backbone polymers, which polymers are ideal, with size proportional to the molecular weight of power 1/2. The entanglement volume fraction $\phi_e$ of the long backbone polymer in in a θ-solvent is:

$$\phi_e \approx \phi^* \left[ N_e(1)^{3/4} / N_{bb}^{1/4} \right],$$

in which $N_e(1) = 32$ is the number of monomers per entanglement strand for PDMS in melt condition, $N_{bb} = 131$ is the number of Kuhn monomers per backbone polymer. The overlapping concentration $\phi^*$ of backbone polymers is:

$$\phi^* \approx v_0 N_{bb} / \left( \frac{4\pi}{3 v_0^{2/3}} \right) b^3 N_{bb}^{3/2},$$

in which $b = 1.3$ nm is the size of a PDMS Kuhn monomer, $v_0 = 6.50 \times 10^{-1} \text{nm}^3$ is the volume of a Kuhn monomer [195]. Therefore, the entanglement volume fraction for linear backbone polymer is $\phi_e \approx 9.1 \times 10^{-2} \cdot 4.0 \approx 0.36$, which is about 6 times of the largest volume fraction $\phi_{bb} \sim 0.06$ used to fabricate the soft elastomers. Thus, the long, linear backbone polymers are not entangled before or after polymerization.

Sylgard 184 is one of the most widely used kits for producing PDMS elastomers. The fabrication of Sylgard PDMS elastomers involves simply mixing the base agent, a mixture of PDMS polymers, and a curing agent that contains both crosslinkers and catalyst, then polymerizing the mixture at 65°C for >6 hours. The polymerized product has a shear storage modulus of $\sim 2,000$ kPa for a typical curing-agent/base mass ratio of 1:10. The gel fraction of the 1:10 Sylgard PDMS elastomer is $\sim 96\%$ (wt/wt). However, the solid fraction in Sylgard PDMS elastomers decreases significantly as the cure agent/base ratio decreases, which is required to achieve lower modulus. For instance, the Sylgard PDMS elastomer with $G' \sim 40$ kPa has only about 50% solid
Figure 8.15: Viscoelastic properties of Sylgard 184 PDMS elastomers. Frequency dependence of storage ($G'$ filled symbols) and loss ($G''$, empty symbols) obtained by classical time-temperature superposition shifts for samples with curing agent/base mass ratio of 1:30 and 1:50. The reference temperature is $-20^\circ$C and the measurements were performed at $-20^\circ$C (red), $20^\circ$C (blue) and $80^\circ$C (green). The shift parameters are the same for all samples: $a_T = 1/9.5$ for $20^\circ$C and $1/3$ for $80^\circ$C; $b_T = 253/T$, in which $T$ is the absolute temperature.

fraction; moreover, the solid fraction becomes negligible, <2%, when the modulus approaching $\sim$1 kPa. In addition, the shear storage modulus of Sylgard PDMS elastomers increases by an order of magnitude as the oscillatory shear frequency increases from $10^{-3}$ Hz to $10^2$ Hz for the sample with curing agent/base ratio 1:50; moreover, the shear loss modulus for this sample becomes comparable to the storage modulus at high frequency $10^2$ Hz, as shown in Fig. 8.15.
Figure 8.16: Time-temperature superposition curves for soft PDMS elastomers. Frequency dependence of storage ($G'$, filled symbols) and loss ($G''$, empty symbols) for different samples obtained by classical time-temperature superposition shifts. The reference temperature is $-20^\circ$C and the measurements were performed at $-20^\circ$C (red), $20^\circ$C (blue) and $80^\circ$C (green). The shifting parameters are the same for all samples: $a_T = 1/9.5$ for 20°C and 1/3 for 80°C; $b_T = 253/T$, in which $T$ is the absolute temperature. Detailed recipe of each sample is listed in Table 8.1.
Chapter 9

The glass transition - droplets, hard particles and microgels

One of the ultimate goals in materials science is to understand how macroscopic properties of materials arise from the structure and dynamics of the constitutive parts. When the underlying structure of the material is crystalline much is known: The existence of such long-range order allows for the prediction of the elastic properties of these solids. However, there exist many technologically important solids that have no long-range order; these include glasses. One of the defining features of glasses is that the microscopic structure of the solid is essentially indistinguishable from that of its fluid: The atoms of a glass-forming liquid slow down until the structure appear arrested. Though this liquid-to-solid transition lacks an obvious, long-range structural signature, it is conjectured that the structural arrest may be related to finer, local structures[211]. Scientific work, both theoretically and less so experimental, has been done to develop measures that quantify mobility with local structure, and our
understanding of the glass transition has improved. By contrast, our understanding of the liquid-to-solid transition of yield-stress-fluids is much poorer. The thermodynamic arguments that explain the arrest of glass-forming liquids do not seem relevant to fluids composed of micrometer scale droplets. Instead, it has been assumed that thermal fluctuations are less important than the network of contacts that is formed when droplets are forced to touch. Nevertheless, because the liquid and solid phases of such emulsions are also disordered, it may be possible to improve our understanding of this transition using tools developed for studying the glass transition. In this chapter, we apply dynamical analyses of three colloidal glassy systems studied with confocal microscopy. This work is ongoing at the time of this thesis’ publication. Additionally, the work presented here is a direct collaboration with Rodrigo Guerra, and also much of the work was performed by excellent students whom I had the pleasure of working with: Eva Sediva from ETH Zurich and Ross Bauer from NYU.

9.1 Colloidal systems

The liquid-solid transition in disordered systems has been studied for emulsion and hard-spheres\cite{6, 212}. However, as this solidification process scales as \((\phi - \phi_c)^n\) where \(n\) is some high power depending on the interparticle potential, the experimental ability to approach \(\phi_c\) is challenging as minute changes in \(\phi\) result in large changes to the sample dynamics, while such changes are far simpler in simulations. To solve this experimental problem, we use gravity to our advantage as a well controlled and constant body force. We prepare samples that are purposely density mismatched such that they cream or settle very slowly, \(< 10\mu m/hr\). By observing the sample
tangential to the body force, gravity, therefore observing horizontally, we are able to capture relative volume fraction changes by transiting vertically. We achieve this by building a confocal which observes individual particles within a sample horizontally, see experimental section for more details. All analyses discussed in this chapter take advantage of the information garnered from individually located and tracked colloidal particles.

Both hard-sphere and emulsion samples are aged for months at constant temperature to avoid changes in the density difference, for details see experimental section and see Fig. 9.2. 3D image stacks of the emulsion system are taken on a spinning disk confocal microscope at different heights every 300 s for 1000 time steps. 3D image stack of the hard-sphere samples are captures using a modified Leica SP5 confocal every 15 s for 2000 time steps, as shown in Fig. 9.1. The emulsions have an opposite relationship of height and volume fraction than the hard spheres: Higher heights correspond to higher volume fractions.

9.2 Pressure scales

The two colloidal samples discussed in this chapter, hard-sphere and emulsion, differ not only in their interaction potentials but also in the pressures that are exerted on them at different heights. The binary emulsions are under much higher pressures than the hard spheres and move significantly smaller distances. It would be advantageous to compare this pressure magnitude quantitatively. The different pressures are also connected to the different volume fractions in the sample. Knowing the volume fraction would give an easier measure to compare our results with the
Figure 9.1: Representative images of core-shell hard-sphere colloids at different heights, 9000µm is this highest height or least pressure. Solidification according to MSD, Fig. 9.3 approximately occurs at 5000µm. Note the change in volume fraction, \( \phi \), with decreasing height and the clean, easy to locate, particle centers in the image due to the core-shell nature of the particles.
Figure 9.2: The mean square displacement illustrating the aging of the 5.3 mm sample. The whole time domain of the experiment was divided into three subsequent time intervals (early, middle and late). The fall in the MSD with time illustrates the aging of the sample.

literature but while relative volume fraction is possible, absolute values of the volume fractions are difficult\[7\]. It would also make the comparison of different colloidal samples with each other easier. Also the comparison of the colloids at the same pressures would bring more insights into their differences. The hard spheres could not be accurately tracked under such pressures, their motion would be optically imperceptible. Therefore another option would be to measure the emulsion under the same pressure as the hard spheres. This would however be a significant experimental challenge.

9.3 Analysis techniques

We use binary sized samples to suppress crystallization. As such, conventional particle locating fails; highly modified GPU-based locating and tracking algorithms
were written by Rodrigo Guerra; detailed explanation is beyond the scope of this chapter. From the individual particle locations and particle tracks several popular method of analysis exist including mean-squared displacement, kurtosis, and 4-point susceptibility.

9.3.1 MSD and kurtosis

Using the trajectories of the particles it is easy to calculate the displacements of each particle $\Delta \mathbf{r}_i(t, t + \tau) = \mathbf{r}_i(t)\mathbf{r}_i(t + \tau)$. Here $\mathbf{r}_i(t)$ is the position of particle $i$ at time $t$ and $\mathbf{r}_i(t + \tau)$ the position of particle $i$ at time $t + \tau$. The second moment of the particle displacement is the mean square displacement,

$$MSD = \langle (\Delta \mathbf{r}_i(t, t + \tau))^2 \rangle$$ (9.1)

The ensemble average here is taken over all starting times $t$ and over all trajectories $i$. The mean square displacement is calculated using the Fourier transform and the convolution theorem $(\mathbf{r}\mathbf{r})(\tau) = \int \mathbf{r}(\tau)\mathbf{r}(t + \tau)d\tau = F^{-1}[\hat{\mathbf{r}}(\omega)\hat{\mathbf{r}}(\omega)]$ and shown for both samples with height in Fig. 9.3 and Fig. 9.4.

The excess kurtosis uses the fourth and second moment of the displacement to measure the deviations from Gaussian behavior. The kurtosis in one direction and three dimensions is,

$$\alpha_2(\tau) = \frac{\langle \Delta x^4 \rangle}{3\langle \Delta x^2 \rangle^2} - 1$$ (9.2)

It is zero for a Gaussian distribution and gets larger with deviations from the Gaussian; values for both samples are shown in Fig. 9.5 and Fig. 9.6. Direct observa-
Figure 9.3: MSD of the binary hard spheres as a function of lag time for different heights (pressures) of the sample. The solid grey line corresponds to slope of one and purely diffusive behavior. Height 3.8mm appears to be more mobile, but this is merely a consequence of an increased number of dimer particles which rotationally diffuse and artificially increase the MSD.
Figure 9.4: MSD of the binary emulsion for different heights (pressures) of the sample. The solid gray line corresponds to slope of one and purely diffusive behavior.

The solid gray line corresponds to slope of one and purely diffusive behavior. This is quantified by the self part of the van Hove correlation function which is computed using the equation 9.1 from the particle trajectories and shown in Fig. 9.7.

### 9.3.2 Susceptibility

The four point correlation function depends strongly on the choice of mobility order parameter. The key point of an order parameter is that when the particle moves away from its position the order parameter falls from one to zero [3]. There have been many suggestions on how to define a suitable order parameter. Many of them involve step or smoothly decaying functions with a cut-off parameter that
Figure 9.5: The kurtosis of the binary hard spheres for different heights (pressures) of the sample as a function of lag time.

defines the length scale of the dynamical heterogeneity. Varying this length scale and the lag time allows us to find the parameters at which the motion of the particles is maximally correlated. We use the mobility order parameter \([213, 214]\),

\[
Q_{t,i}(a, \tau) = \exp\left(-\frac{\Delta r_i(t, t+\tau)^2}{2a^2}\right)
\]  

(9.3)

Here \(\Delta r_i(t, t+\tau)\) is the displacement of drop \(i\) between \(t\) and \(t+\tau\). The susceptibility is then defined as,

\[
\chi_4(a, \tau) = \langle Q_i(a, \tau)^2 \rangle - \langle Q_i(a, \tau) \rangle^2
\]  

(9.4)

With, \(Q_i(a, \tau) = (1/N) \sum_{i=1}^{N} Q_{t,i}\) with \(N\) being the number of particles. We calculate only the self part of the 4-point susceptibility which has been shown to be the
Figure 9.6: The kurtosis (equation 9.2) of the binary emulsions for different heights (pressures) of the sample as a function of lag time. The inset zooms into the region of long lag times.
Figure 9.7: The self part of the van Hove correlation function in the x direction for the (left) binary hard spheres (5.3 mm, $\tau = 1250$ s) and the (right) emulsion (2 mm, $\tau = 3 \times 10^4$ s). The red dashed lines correspond to a single Gaussian fit and the red solid lines to an exponential.

dominating term[215].

9.4 Discussion

The MSDs of the hard spheres in Figure 9.3 show the characteristics of a glassy material. There is a plateau in the displacement at intermediate lag times. This is due to the trapping of particles in a cage of their neighbors. At short time scales their motion is diffusive and their displacements not long enough to break the neighbor cage. Only on longer timescales does the mean square displacement increase linearly again as the particles are able to escape their cages. The higher the volume fraction or the deeper the sample the longer is the plateau of the cage trapping. The hard
Figure 9.8: (left) $\chi_4$ as a function of lag time and the length parameter $a$ for the hard spheres at 5.3 mm. (right) $\chi_4(\tau, a^*)$ and the order parameter $Q(a^*, \tau)$ of the hard spheres at 5.3 mm as a function of lag time. $\chi_4$ and $Q$ are plotted here at $a^* = 0.41 \mu m$ which maximizes the susceptibility.

Figure 9.9: (left) The 4-point susceptibility as a function of lag time and the length parameter $a$ for the emulsion at 2 mm. (right) The 4-point susceptibility and the order parameter $Q(a^*, \tau)$ of the emulsion at 2 mm as a function of lag time. $\chi_4$ and $Q$ are plotted here at $a^* = 0.036 \mu m$ which maximizes the susceptibility.
spheres in Figure 9.3 have the end of the plateau of the MSD at the peak of the kurtosis. As diffusive behavior begins the kurtosis descends to zero. The peak of the \( \chi_4(\tau, a^*) \) is slightly shifted from the kurtosis peak as shown in Fig. 9.8.

The emulsion in Figure 9.4 exhibits a strikingly different behavior and linear behavior. This may imply pure Fickian response, but the displacement distribution significantly deviates from a Gaussian, as seen in Fig. 9.7. This behavior has been recently observed in several experimental systems and has been termed anomalous yet Brownian diffusion.

Both the hard spheres and the emulsion exhibited a clear peak in \( \chi_4 \) which is a manifest of the existence of a dynamical heterogeneity in the systems. However activated diffusion (caging) cannot be assigned as a underlying mechanism for the dynamical heterogeneity in the emulsion. The mechanism of a dynamical heterogeneity in a system where activated diffusion might not take place as in our emulsion is still not clear. This open question should be a subject of further investigations. The binary colloidal emulsion has proven to be an interesting glassy model system with unconventional dynamics. Further studies with the emulsion could generalize and clarify the concept of dynamical heterogeneity in glassy systems and further develop the concept of jamming.

Ongoing experiments include expanding this experimental exploration to microgel particles which do not have a harmonic or hard-sphere potential, but most closely resembles a Hertzian response. To this end, the crosslinking density of the microgel system is being controlled to explore how particle stiffness affects the liquid-solid process.
9.5 Experimental for this chapter

9.5.1 Hard-sphere synthesis

Hard-sphere colloids consist of a core-shell structure where only the core is fluorescently labeled. The shell is density matched with the continuous phase so that only the core causes sedimentation. The particles are synthesized in two steps. First the core is dispersion polymerized and the shell is then formed around with seeded polymerization. The core is polymerized from an index matching molar ratio of trifluoroethyl methacrylate and methy methacrylate and polymerizable fluorescent dye, Cy3MM, see Chapter 2 and 3 for more details. The shell is composed of a refractive index matching molar mixture of tert-butyl methacrylate and trifluoroethyl methacrylate. The continuous phase is a refractive index matched mixture of primarily formamide and sulfolane, with DMSO added drop wise until the mixture is also density matched to the shell polymer. The density difference in this system is about 10 kg/m$^3$. The sample is prepared from a 1:1 number ratio of 1.24:1 diameter large and small particle batched synthesized using the same core particles thus have nearly equivalent buoyant masses.

9.5.2 Microgel synthesis

Microgel particles consist of a core-shell structure where only the core is fluorescently labeled. The synthesis proceeds in two-steps. The cores are first synthesized by surfactant-free emulsion polymerization with the ratio of trifluoroethyl methacrylate to N-isopropyl acrylamide is kept constant at 60:1; a small quantity of Coumarin 7
dye is added. The resulting core particle are \(2r \sim 550\text{nm}\). This core particle dispersion is dialyzed for several days. The poly N-isopropyl acrylamide shell is added in a similar fashion to [216], but here a 60ml syringe operates at 1ml/minute containing all the monomers while the core particle are located in the reaction flask. Core-shell microgels of 1-2.8\(\mu\)m diameter may be formed by adjusting the ratio of monomer to core particles and the amount of crosslinker. The sample is prepared from a 1:1 number ratio of 1.24:1 diameter large and small particle batches synthesized using the same core particles thus have nearly equivalent buoyant masses. Additionally, three different degrees of crosslinking are prepared to test relative particle stiffness.

### 9.5.3 Emulsion synthesis

The emulsion droplets are dispersion polymerized poly-N-butyl acrylate, a low Tg polymer [217]. Droplets are washed several times in water and then dispersed in the continuous phase, pure DMSO which nearly perfectly index matches the droplets. To increase the density difference between droplet and continuous phase, we use fully deuterated DMSO-D6, which yields density difference of 110kg/m\(^3\) between the droplets and the continuous phase. The sample is prepared from a 1:1 number ratio of 1.24:1 diameter large and small particle batched synthesized using the same polymer. As these particles do not have equivalent buoyant masses, the sample is loaded at \(\phi = 0.40\) to minimize and size segregation during creaming.
9.5.4 Horizontal confocals - Yokogawa and Leica

Two versions of horizontal microscopes are designed for long-term and short-term imaging. The long-term horizontal confocal is constructed around a Yokogawa CSU22 spinning disk confocal. The instrument includes a Leica tube lens, Leica microscope objective - 63X oil immersion located at the parfocal distance, a piezo-objective control, PIFOC P-725, and a PCO edge.5.5 CMOS camera, as seen in Fig. 9.10 and 9.11. The instrument is controlled entirely by Matlab running a simple loop script which captures a single stack. The sample is mounted in a fixed 3-axis translation stage; crucially, in the gravity axis a 2 inch Newport translation stage is use to fully translation over the entire sample.

The short-term horizontal is modified from a Leica SP5 confocal. The objective is ‘extended’ and turned using a 90 degree fixed mirror all within a lens tube. The z-translation galvo stage of the confocal is mounted vertically and the sample attached. By translating the x-y stage, the sample may be brought into focus while z-stacks are captured by translating the galvo stage and different heights accessed by translating the objective turret, see Fig. 9.12 and Fig. 9.13 for more details.

During this project, sample chambers became a nuisance due to the long equiliibration times necessary for glassy aging and slow imaging. While many forms of glues and epoxies were explored, along with metal and plastic vessels, the best sample chamber for long term imaging is the classic one - flame sealed glass tubes with glass thickness being approximately the thickness of coverslips, ∼ 200µm. These capillary tubes are purchased from Vitrocom. For ideal imaging, a glycerol immersion objective is used to index match the sample, glass capillary, and immersion fluid.
Figure 9.10: The emulsion sample is mounted vertically on a 3-axis translation stage. Different heights are accessed by translating the 3-axis stage vertically while the sample is brought into focus by translating the stage into the objective.
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Figure 9.11: A closer view on the sample and the microscope objective.
Figure 9.12: Leica SP5 confocal with the sample mounted vertically along with the z-galvo stage.
Lastly, and of absolute importance, each sample on both confocal is highly temperature controlled to better than ±0.1°C using a homemade Peltier system controlled by a ThorLabs TEC. While thermal energy changes only minutely over ‘room temperature’ fluctuations, the density difference due to the solution’s expansion coefficient causes does change to a degree and warrants rigorous temperature control.
Chapter 10

Conclusion

This thesis explored several colloidal phases including gels, glasses and crystals in Chapters 4, 5, 6, and 9. Of particular focus was the mechanical failure of colloidal gel stability by external or internal forces. I have discussed how gel stability is directly coupled to its mesostructure and additionally to the microscopic contacts between individual particles. While there are many observations in the literature of gel failure, these two crucial aspects have generally been overlooked and help unify the wide ranging observed mechanical responses. Currently still poorly understood is delayed collapse: A colloidal gel experiencing a gravitational stress due to a buoyancy mismatch between the colloid and suspending fluid, but tentatively does not collapse until hours, days or weeks later. The material response to this stress is complex as it involves not only shear, but also syneresis and compression. Additional, hydrostatic forces due to the solution back-flow through this porous media, must not to be neglected; this flow has been shown to rearrange the gel mesostructure in the flow directions[133]. I also investigated this phenomena, but could not definitely eluci-
date the origin of this delay; one key finding is that the boundary conditions had a profound affect. Specifically, completely eliminating wall adhesion, similar to the syneresis work, appeared to eliminate any delay; the gel immediately collapsed. The origins of this delay is most likely a complex combination of mesostructure, syneresis, and adhesion to the container walls; further experimentation is warranted and should couple both macroscopic, mesoscopic, and microscopic investigation.

Also included in this thesis are several chapters that focused on colloidal chemistry, 2 and 3. These chapters detail the synthesis of two new colloidal model systems dispersed in low and high dielectric constant solutions. Each system has its merits. Long screening lengths are easy to achieve between PMMA colloids dispersed low dielectric constant solution, as such, with increasing $\phi$ the dispersion transitions to a body-centered cubic crystal phase, unlike hard-spheres which form a face-center cubic crystal. By contrast, the colloidal system dispersed in high dielectric solution is highly flexible; by manipulating the monomer ratio, these copolymer particles can be tuned to have no density difference compared to the solution, or a high density difference enabling sedimentation, all while maintaining a constant refractive index. Additionally, the incorporation of ATRP into colloidal synthesis permits nearly infinite control in the surface chemistry. As discussed in the introduction, colloidal model systems should be manipulated to explore a particular physics question. In my experience, the inflexibility of existing systems limits or greatly hinders the effectiveness of experimentation.

Lastly, this thesis discusses how siloxane chemistry may be used to the Soft Matter physicist’s advantage. Chapters 2 and 8, both use reactive forms of PDMS purchased
Chapter 10: Conclusion

from commercial sources. While this century has been called the age of silicon, its polymeric form, PDMS, is an often overlooked crucial component of this revolutionary change to society, as PDMS finds application in medical devices, personal care products, and electronics to name only a few. As such, the commercial availability of siloxane polymers continues to grow with ever increasing functionality. Comparable to the recent revolution in optical microscopy being driven by biological sciences, soft matter applications are not the driving force for this siloxane chemistry but it may be exploited for our own needs.
Bibliography


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