HOW TO RELAX

Dynamics in Colloid Polymer Composites During Syneresis

QIMENG WU

Propositions

1. Particle nature influences stress relaxation of colloidal materials.
(this thesis)
2. Allowing a material to fail is an indispensable path to the understanding of the underlying cause.
(this thesis)
3. Boundary conditions complicate interdisciplinary research as they do in study of colloidal gel mechanics.
4. The development and commercialization of immersive virtual reality can revolutionize how scientific advances are popularized.
5. There needs to be more incentives in being a peer reviewer, besides the self-rewarding feeling in defending the truth of science.
6. To take one step further in gender equality beyond acknowledging that women can achieve as much as men is conceding that women can stumble as much as men.
7. Chinese shops in middle-sized European cities are like time machines, reflecting the suspended perceptions of a foreign culture.

Propositions belonging to the thesis entitled:

How to Relax

Dynamics in Colloid Polymer Composites during Syneresis

Qimeng Wu

Wageningen, 9 November 2020

HOW TO RELAX

DYNAMICS IN COLLOID POLYMER COMPOSITES
DURING SYNERESIS

QIMENG WU

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DYNAMICS IN COLLOID POLYMER COMPOSITES

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QIMENG WU

Thesis

Submitted in fulfillment of the requirements for the degree of doctor
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“TO SEE A WORLD IN A GRAIN OF SAND,
AND A HEAVEN IN A WILD FLOWER,
HOLD INFINITY IN THE PALM OF YOUR HAND,
AND ETERNITY IN AN HOUR.”

William Blake “Auguries of Innocence”

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CHAPTER 1

Introduction

When a material is under stress, it tends to relax. Relaxation elicits alterations in material mechanical properties, which can result in instability. The aim of this thesis is to understand a specific mechanical failure known as syneresis, i.e. the contraction of the material accompanied by the expulsion of fluid. Syneresis is a typical mechanical instability mostly encountered in food products which are colloid-based soft solids. In this thesis we explore the underlying physics governing syneresis in colloidal materials via investigating constituent particle dynamics at multiple length scales. We extract the problems to their basic elements and design model food systems, and more fundamental colloid-based models to study physics governing syneresis in detail and provide new fundamental insights. In the following, we provide a brief introduction and context to the thesis.

1.1 Colloidal Domain

Colloids Are Everywhere

Colloids consist of nanometer to micron sized objects that form a dispersed phase when suspended in a continuum phase. Depending on the states of matter involved, we can distinguish colloidal sols, emulsions, foams, aerosols, solid suspensions, porous materials and solid foams. Manifestations of the colloidal domain surround us every day. In nature, colloidal systems are omnipresent: gas dispersed in liquid gives foam; solid and liquid dispersed in gas give smoke and fog, respectively. Many of our daily commercial products involve colloidal systems as well: production of porous plastic, paint, lubricants, home and personal care products such as shampoo, cosmetics, skin creams, toothpastes and

Figure 1.1: Colloidal domain in nature (a) fog in a misty forest; (b) foam on the surface of a polluted river; (c) volcanic smoke and in commercial products (d) carbon fiber reinforced plastic; (e) paints on a palette; (f) ice cream. Adobe Stock licensed.

detergents, as well as food products such as tomato ketchup, sauce, mayonnaise, yogurt, margarine, and ice cream. A few examples are illustrated in Fig. 1.1.

The fate of a colloidal system is determined by volume fraction and inter-particle interactions. When particles are repulsive to each other, they stay apart, resulting in dispersions that are stable against aggregation and, at higher volume fractions, in glassy and crystalline states. An attractive interaction between the particles induces aggregation and the formation of clusters or gels, or to liquid-liquid phase separation. By tuning the interaction potential and volume fraction together with parameters like, external stresses, polydispersity, particle softness, etc, a variety of phase behaviour of colloidal system can be obtained and the stability of the colloidal systems can be altered [1, 2].

The diversity in phase behaviour and its tunability play a crucial role in many processes. For instance, many commercial products mentioned earlier, such as, hair gel, water-based paint, milk, mayonnaise and pharmaceuticals, rely on colloidal stability in certain ways to maintain homogeneity in the product. In addition to the involvement in the existing application, the ability to control the colloidal domain sheds light on various challenges in technology, for instance, in designing materials with rapid and reversible transition between solid and liquid behaviour (injectable pharmaceuticals, drilling fluids, and flexible body armor), fabrication of novel high strength composite materials and more sustainable food

processing and product development [3, 4].

Food Colloids and Soft Matter

A considerable number of natural and processed food systems are colloidal in nature, i.e., they comprise of colloidal particles (emulsion droplets, gas bubbles, fat crystals, ice crystals, etc.), food-grade biopolymers (proteins and polysaccharides), dispersed in an aqueous phase with low-molecular weight ingredients (mineral salts, sugars, surfactants, etc.) [5]. Food systems are characterised by their structural complexity on many different length scales, ranging from the molecular to the macroscopic scale. Many manufactured foods contain multiple dispersed phases. Fig. 1.2 illustrates the microstructure of mayonnaise, yoghurt and cheese. Mayonnaise is an oil in water emulsion comprised of dispersed oil droplets, stabilized by egg yolk proteins and phospholipids, in a continuous aqueous phase. Yogurt, made from heat-treated milk above 85°C, comprises of a network constituted by casein micelles forming branched chains, triggered by lowering the pH via fermentation with lactic acid bacteria and fat droplets dispersed in a continuous phase containing whey protein. By contrast, cheese is made from unheated milk with proteolytic enzymes, resulting in a gel consisting of connected casein micelle clusters and large void spaces before cutting [6].

The colloidal length scale is commonly set for food structuring since this length scale coincides with what humans can sense with the tongue [7]. More importantly, the building blocks in food colloids, which are significantly larger than an atom but much smaller than the overall dimensions of the sample, have physical interactions which are typically weak, on the order of the thermal energy, $k_B T$. As a consequence, these materials have low elastic moduli, leading to low resistance to deformations and therefore a soft appearance, and they can be subjected to flow, which is crucial for food intake and digestion. In physics, food is commonly regarded as a kind of soft condensed matter. Aside from softness, there are many other properties that are also induced by the size of the constituent building blocks. Here we list a few more features of soft matter: (i) the properties of soft matter are largely independent of the chemical details of its constituents, which is due to the large separation of the length scales of the mesoscopic structures and the chemical moieties at the molecular scale; (ii) due to the

Figure 1.2: Food Colloids and their microstructure (a) mayonnaise, (b) yoghurt, (c) cheese, (d) Confocal microscopy image of distorted oil droplets in mayonnaise; the continuous aqueous phase and the interface are fluorescently labelled of Nile Blue. Reprinted with permission from [12]. (e) Electron microscopy image of yogurt protein matrix, made from defatted milk, composing of casein particles and attached κ -casein- β -lactoglobulin complexes in the form of branching chains. Two streptococci are shown in yellow. The scale bar represents $2\ \mu\text{m}$. Reprinted with permission from [6]. (f) Electron microscopy image of whole milk coagulated for cheese production before cutting. Fat globules are marked yellow. The scale bar represents $5\ \mu\text{m}$. Reprinted with permission from [6]. (a-c) Adobe Stock licensed.

inhomogeneity in length scale of nanometers to microns, soft matter systems usually have a very large internal interfacial area, which makes the interfacial chemistry important; (iii) the weak interactions between the building blocks imply that thermal energy plays an essential role. The constantly Brownian motion makes entropy and fluctuations relevant to soft matter systems [8, 9].

Modification of the surface properties (interaction potential) or bringing the food colloids into a kinetically arrested state impart food product shelf and handling stability [10, 7]. Extensive effort has gone into studying the stability of food colloids focusing on the nature of chemical constituents in food colloids, e.g., exploring the effect of different types of surface stabilizers and varying compositions of the chemical constituents [11]. In this thesis, we focus on keep-

ing food colloids mechanically stable from the soft matter physics approach, by coarse graining, i.e. ignoring chemical details at the molecular scale up to the level that similarities in the physical behaviour emerge. Rather than investigating the chemical constituents themselves, we look into the physical consequences of chemical alterations. By looking into the dynamics of the basic components of food colloids of different nature and with different strength of the interactions, we aim to reveal the mechanisms underlying the formation and breakdown of these materials, and hope to facilitate the prediction, optimization and improvement of food colloid processing conditions, and the shelf life of relevant products.

1.2 Soft Colloidal Solids

In this section, we introduce typical approaches in food colloids to impart them rigidity. The operative definition of a solid is a material that has a finite elastic modulus. In other words, a material that exhibits rigidity [13]. Phase transitions from a liquid to a solid or solid-like behaviour observed in colloidal systems can commonly be achieved via three mechanisms: (i) colloidal crystals and glasses driven by entropy in systems dominated by repulsive interparticle potential; (ii) colloidal gels mediated by attractive interactions between the particles and (iii) Composites comprising of colloids and non-interacting polymers by modifying the viscoelastic properties of the continuous phase.

Colloidal Crystals and Glasses

For the formation of colloidal crystals and glasses, we consider the “hard sphere” scenario, i.e., the impenetrable spherical particles have no attractive nor repulsive interactions. In this case, the phase behaviour is purely controlled by entropy, see Fig. 1.3 (a). Below the freezing point, $\phi = 0.494$, particles in colloids undergo Brownian motion, resulting in a disordered dispersion, which behaves like liquid. With increasing $\phi > 0.494$, a crystal phase appears, leading to an abrupt transition in the phase diagram where there is the coexistence of “liquid” and “solid” phase. At $\phi > 0.54$, hard sphere colloids form a crystalline state in which the particles are organized in a highly ordered regular array, as shown in

Figure 1.3: (a) Schematic phase behaviour of colloids comprising monodispersed hard spheres as a function of volume fraction, ϕ . Dashed arrows indicate equilibrium states, whereas solid arrows are non-equilibrium states. (b) Confocal microscopy image of a colloidal glass in a colloidal dispersion with 5% polydispersity. Scale bar represents 10 μm . Reprinted with permission from [2]. (c) Scaled low shear viscosities at different ϕ for various colloidal suspensions of nearly monodisperse hard spheres. The low shear viscosities (η) are normalized by the viscosity of the pure solvent (η_0). The line is a fit to the Doolittle equation, which was first used to describe the temperature dependence of viscosity in molecular liquids approaching the glass transition [23]. Reprinted with permission from [2]. (d) Bright-field image of the NIPA particle colloidal crystal; Scale bar represents 5 μm . Each bright spot corresponds to the central region of a 0.75 μm diameter particle. Reprinted with permission from [24].

Fig. 1.3 (d). The formation of long-range order indeed decreases configurational entropy. However, this entropy reduction is counteracted by an increased free volume available for local motion in the crystalline state, which increases the entropy. At high volume fractions the latter dominates and the overall increase in entropy drives the crystallization.

The phase behaviour described above corresponds to equilibrium conditions, dashed line in Fig. 1.3 (a) with a final state corresponding to the global minimum of free energy. Crystallization in colloids requires the particles to have a rather narrow size distribution. Conditions like high polydispersity of the particles can strongly hinder the formation of a close packed crystal structure, leaving colloids trapped in a local minimum of free energy, forming a disordered state known as glass. The glass transition for hard spheres, occurs around $\phi_g \sim 0.58$, showing the lack of any obvious order (Fig. 1.3 (b)) and standing in contrast to the ordered nature of the colloidal crystal shown in Fig. 1.3 (d). Even though the structure of a glass remains liquid-like, the particle volume fraction is high enough to induce microscopic dynamic arrest by particle crowding; the free volume surrounding each particle decreases and the particle motion becomes increasingly restrained by neighbouring particles due to the formation of configurational cages [14, 15, 2]. This microscopic slowing down of relaxation dynamics in colloidal glass manifests macroscopically as a sharp increase in viscosity. Above ϕ_g , a small increase in volume fraction can result in a viscosity increase of orders of magnitude, see Fig. 1.3 (c) [16, 17, 18]. At the appropriate time scales, a phase with an exceedingly high viscosity can be considered as a solid for most practical purposes [19, 18]. Thus, glasses resist shear deformation, which gives them a finite shear modulus [20]. Please note, that the debate whether the glass transition is the true liquid-solid transition remains unsettled and is beyond the scope of this thesis [21, 22].

Colloidal Gels

Moving away from purely repulsive spheres, interparticle attraction forms another route to obtain a kinetically arrested phase: a colloidal gel, which is a soft solid comprising of two intertwined phases: a solid network and a liquid solvent. Attraction mediates the formation of clusters of particles. At sufficient volume fraction of particles and attraction strength, a space-spanning network forms, in which a particle-rich phase of the phase-separating dispersion becomes dense enough to form a glass (Fig. 1.4 (a)). Gelation is characterized by an arrest in particle dynamics and the onset of elasticity [25, 1, 26, 27]. Such colloidal gels derive their rigidity from physically bonded particles which form strands and

Figure 1.4: (a) Phase behaviour of a colloidal system with attractive interparticle potential U and colloid volume fraction ϕ . (b) Schematic illustration of depletion attraction; polymer coils (green) are excluded from a depletion zone of thickness L (lilac) near the surface of the colloidal particles. [38]

connecting nodes that develop into a percolating elastic network [28, 29, 30].

When electrostatic repulsion is screened by adding salt or by changing the pH of the continuous phase of colloids, particles can come together and stick to form clusters via van der Waals forces. As the van der Waals forces are much greater than thermal energy, $U(r) \gg k_B T$, one generally refers here to “strongly attractive” systems. Commonly, particles in colloids have a surfactant or polymer layer grafted to their surface to stay sterically stable, which keeps the particles far enough from each other without interacting via van der Waals attraction.

Another common attractive interaction between particles is through a polymer-induced depletion interaction (Fig. 1.4 (b)). Depletion interactions arise when the continuous phase of the colloids contains non-adsorbing particles, called depletants, which are intermediate in size compared to the size of the dispersed particles and the size of the solvent molecules. The most common depletants are dissolved non-adsorbing polymer molecules. For the center of mass of the polymer coils to approach the particle surfaces, the coil must substantially deform, which reduce the configurational entropy of the polymer. As a consequence, around each particle there is a depletion zone of thickness, L , approximately equal to the polymer radius of gyration R_g , from which polymer is excluded. Due to the depletion zones, there is a decrease in the total accessible volume for the polymer. As a result, the free energy increases by $G_{dep} =$

$V_{dep}\Pi_{pol}$, with Π_{pol} the osmotic pressure of the polymer solution and V_{dep} the total depletion volume. When the depletion zones of two particles overlap, the resulting decreased depletion volume leads to an increase of the entropy of the system and a reduction of the total free energy by $\Delta G_{dep} = -V_{ov}\Pi_{pol}$, with V_{ov} the overlap volume. This results in an attraction between the particles, which is typically weak, $U(r) > k_B T$ [31, 8]. The range and strength are set by the size ratio of the depletant and the particle and the concentration of the depletant.

Van der Waals and depletion attractions lead to a variety of disordered arrested states, which can generally be reached through two routes: (i) Diffusion Limited Cluster Aggregation (DLCA) or (ii) Spinodal Decomposition. At sufficiently high attraction, colloidal gels are constructed via DLCA, where once particles collide, they are irreversibly bound to each other and clusters are rapidly formed without further rearrangement [32]. These clusters are fractal in structure, aggregate upon collision and ultimately grow to form a space-spanning network. Trapped particles suppress possible rearrangement of the network, leading to thin and highly branched strands in these gels [33]. At lower attraction, gelation is achieved via a mechanism known as spinodal decomposition; the colloid will tend to separate into particle-rich and particle-poor phases once it is above some critical volume fraction due to concentration fluctuations of each phase [34]. When the particle-rich phase becomes large enough to form a space-spanning network, kinetic entrapment is reached, which significantly slows down further demixing. The possible rearrangements of the particles in the strands of the network result in thicker strands than the ones in DLCA gels. It has been shown in a number of works that the phase separation process will be arrested when the density of the colloid-rich phase reaches that of a colloidal glass [35, 36, 37, 26, 27]. Under conditions where the particle-rich phase forms an interconnected network, the glassy arrest of the particles within the network naturally entails gelation.

Composite Soft Solids

Another quintessential soft colloidal solid is obtained by making composite materials. A composite material consists of two or more materials that are combined on a macroscopic scale to form a useful third material. The advantage of

composite materials is that, if well designed, they usually exhibit the best qualities of their components or constituents and often some qualities that neither of their components possess. Particulate composite materials, achieved by adding thickeners to food colloids, have abundant applications in food structuring [39, 11]. Thickeners are very often incorporated in the continuous phase of food colloids for the desired texture and mechanical stability, especially in low-fat products. Water-soluble (bio)polymers like polysaccharide and protein are typical examples of thickeners, for instance, starch [40]. Starch is a complex composite system itself, comprising of amylose and amylopectin [41]. When heating in water, the starch suspension converts into a turbid viscoelastic paste, in which water-soluble individual polymers, water-swollen starch microgels, and water-insoluble granules coexist [42]. A network consisting of an amylose matrix with deformable swollen granule fillers develops at sufficiently high starch concentrations [43]. The addition of such edible biopolymers into food colloids can lead to the emergence of complex physical changes, e.g. a significant increase of the viscosity in the continuous phase and glassy behaviour of the particles, arriving at solid-like behaviour for practical time scales [11]. Looking beyond food applications, polymer melts containing hard nanoparticles have been studied extensively in virtue of their technological importance in batteries, sensors, and implants [44]. Rheological properties of such composites depend very sensitively on the polymer-particle and particle-particle interactions [45, 46]. Also well studied are soft composites of rigid colloidal particles mixed with soft particles, such as microgels [47] or star polymers [48, 49]. The difference in softness between the two types of particles defines the penetrability between them, resulting in distinctly unique interactions which give rise to a rich phase behaviour [50, 51, 52].

1.3 Dynamics at Multiple Length Scales

Mechanical Instability

Soft colloidal solids are often subject to transient deformation in numerous steps during their processing and handling. Understanding the mechanical response to various stresses of these materials is of paramount importance to predict and control the properties of many applications. Due to their softness, such solids can

Figure 1.5: (a) Snapshots of a colloidal gel at several instants during the delayed collapse in simulations. Reproduced from [4] with permission from The Royal Society of Chemistry. (b) Evolution of the anchored gel microstructure at $\dot{\gamma} = 9 \times 10^{-3} s^{-1}$ (upper panel) and $\dot{\gamma} = 3.5 \times 10^{-2} s^{-1}$ (lower panel). The structures are represented at $t = 0, 255, 610, 1088 s$ after the onset of shear. The scale bar represents $7.5 \mu m$. Reproduced from [54] with permission from The Royal Society of Chemistry. (c) Syneresis after cutting the casein gel during cheese-making, releasing whey. Syneresis after scoop (d) in yoghurt and (e) in low-fat mayonnaise. (c) Adobe Stock licensed.

exhibit a solid-like to liquid-like transition under imposed forces and fields. The resulting complex viscoelasticity is intimately coupled with their microstructure and internal dynamics [53]. Therefore, quantitative descriptions of the microstructure and dynamics of such colloidal solids are crucial to reveal the mechanisms accounting for the desired mechanical properties. There has been sustained attention in studies on elucidating mechanics of colloidal materials, especially colloidal gels, under gravity and shear.

Once a colloidal gel forms, the heterogeneous structure, often bonded through weak non-covalent interactions, e.g. depletion, is immediately subject to gravity. After an initial period of delay during which the gel can support its own weight, the gel may collapse suddenly, owing to gravitational stress to form an unstructured sediment at the bottom of the container. This delayed gravitational

yield has been observed for gels made from a variety of materials, and for a wide range of attraction strengths [55, 56, 57, 58]. Three macroscopic sedimentation regimes characterize the delayed collapse: an “induction period” with relatively slow initial compression, after which the gels abruptly undergo significant restructuring and fast sedimentation, followed by a final compression with decreased sedimentation rate to an equilibrium height [56, 59, 60, 61]. Previous studies on understanding and developing predictive models propose two widely discussed perspectives: (i) evolving boundary conditions between the gel with the container leads to the gel collapse [62, 63, 55, 64]; (ii) collapse is attributed to bulk rheological evolution; for strong gels of which particles are not allowed to escape, gel collapse is associated with the solvent backflow that ruptures the network [58, 65, 59, 60]. When attraction between particles is on the order of $k_B T$ and the volume fraction of the dispersed phase is low enough, gels are made from particles connected with reversible bonds. Collapse in such weak gels is related to aging which results in structural and rheological changes that weaken the gel. Recently, large-scale simulation shows that the delayed collapse bears the hallmarks of a “mechanical phase transition” from an arrested phase toward a more dense structure as seen in Fig. 1.5 (a) [4].

When sheared, soft colloidal solids yield and exhibit liquid-like behavior. Detailed studies on colloidal gels have shown that the duration of the yield event, the subsequent material stress, and post-yield flow behavior are dependent on the initial microstructure and the elastic response of the material [28, 66, 67], which are determined by particle volume fraction [68] and the strength of interactions between particles [69]. Experiments with shear confocal microscopy have defined a three-step manner of shear-induced yielding of gels at moderate shear rate: an early rise in stress with a highly anisotropic network oriented near the extensional component of the shear flow field, a yield point, and long-time flow comprised of dense disconnected clusters, depicted in Fig. 1.5 (b) [54, 70]. For dilute colloidal gels formed with interparticle bonds that are strong enough to be indifferent to thermal fluctuations, yielding has been attributed to the solid-like fracture of the strongly bonded network [71, 72]. In terms of the yielding of dense, reversible gels, there is an initial yielding at a yield strain on the order of a bond length, followed by a secondary yield event during flow start-up [68, 69].

In contrast to the previously discussed yielding of a solid network and fluidization of a gel induced by applied strains, a material that experiences syneresis does not necessarily undergo a solid to liquid transition. For instance, when scooped, yoghurt and low-fat mayonnaise do not flow as a whole but retain the shape of the scoop where fluid accumulates. During cheese production, after knifing, while whey is being expelled, the casein particles remain connected in solid gel structures, as depicted in Fig. 1.5 (c-e). Besides food products mentioned in the beginning of this chapter, syneresis detrimentally affects other colloid-based materials ranging from ceramics to composites as well.

Syneresis has been observed in colloidal gels consisting of attractive soft particles in an adhesive container; the strong anchoring of the gel to the container walls results in tensile stresses building up in the sample due to the decrease of the interparticle distance. When gently spun, the colloidal gel detaches without breaking, exhibiting syneresis [73, 74]. During the formation of a colloidal gel, local compaction occurs, driven by a tendency to reduce interfacial energy and its inhomogeneity results in random regions of higher deformation; because the gel is elastic, there is a displacement field around each of these deformations. These inhomogeneities can then be considered as localized internal stress built within the network [73, 30]. When this internal stress is of sufficient amplitude, colloidal gels that are allowed to detach from the container walls undergo syneresis which can be amplified by external stresses.

When syneresis occurs, the bulk material compaction and fluid expulsion are triggered at the microscopic scale by entropic and other interactive stresses that control particle rearrangements that ultimately cascade to the macroscopic length scale. To understand the nature of these local rearrangements that drive syneresis in a colloid based material, a study of local particle dynamics is needed. By investigating the microstructure and dynamics at multiple length scales, both for model soft solids and real food products, we strive to understand the underlying physics governing how stress is relaxed during syneresis. With this we hope to better facilitate the prediction and improvement of mechanical stability of food colloids for application purpose, as well as to add knowledge about the complex mechanical response of soft solids.

Interestingly, syneresis is observed mostly in gels with liquid droplets as the

Figure 1.6: (a) Probability distribution of individual particle displacement; the non-Gaussian shape is clearly visible by comparing the experimental data (open circles) with the Gaussian fit (dashed line). The solid lines are exponential fits to the distribution. (b) Computer render of an experimental dense liquid. The 10% most dynamic particles are rendered as large spheres with the rest as small spheres. It is clear that the dynamics are highly heterogeneous as most dynamic particles in the system form clear clusters. Reprinted with permission from [75]. (c) Individual particle mean square displacements at $\tau = 498$ s versus Z from experiments (symbols) and the model described in the text (solid lines) for $c_p = 30.9$ mg/ml (diamond), 34.1 mg/ml (circle), and 34.6 mg/ml (square). Reprinted with permission from [76].

dispersed phase, as found in most colloid-based consumer products and food materials. Yet, most studies on colloidal dynamics have been conducted on solid particle based materials, in which syneresis occurs much less frequently. Therefore in this thesis, we focus mainly on understanding the dynamics in liquid particle based materials.

Dynamics at the Individual Particle Level

Interestingly, even in the absence of external stresses, colloidal gels undergo slow internal rearrangements that cause the network structure to gradually age and coarsen [77, 78], which can ultimately lead to macroscopic changes, for example, in the long-term stability of products against syneresis. The mean-squared displacement, $\langle \Delta r^2(\tau) \rangle$, is a common measure for the time and ensemble averaged mobility of the particles in a dispersion. In the hard-sphere limit of colloids, at low volume fraction and low attraction strength, $\langle \Delta r^2(\tau) \rangle$ exhibits linear dependence on the lag time τ , obeying, $\langle \Delta r^2(\tau) \rangle = 6Dt$, where D is the diffusion coefficient.

As the volume fraction or attraction strength increase, the simple diffusive

behaviour gives way to more complex dynamics. Often, the ensemble and time averaged $\langle \Delta r^2(\tau) \rangle$ fail to capture the emergent temporal and spatial heterogeneous dynamics. When the coordinates and trajectories of all particles are explicitly known, from computer simulation or by applying particle-tracking algorithms on microscopy data of colloids imaged at the individual particle scale, dynamics of particles at individual particle scale can be computed. For glassy materials, based on displacement of particles resolved at individual particle level, the probability distribution of particle displacements as characterized by the self-part of the van Hove correlation function can be calculated. As illustrated in Fig. 1.6 (a), these distributions show significant deviations from the Gaussian distribution expected for Brownian motion; they exhibit exponential tails, in addition to a central Gaussian region. This non-Gaussian behaviour in the van Hove correlation function indicates that the dynamics in such systems is characterized by short-time rattling of particles within the cages formed by neighbouring particles and occasional cage rearrangements, which involve a cooperative motion of multiple particles. These cage-breaking events give rise to dynamic heterogeneity [79, 80, 75, 81, 82]; despite the spatial vicinity between regions of particles, they may exhibit hugely distinct dynamics, as depicted in Fig. 1.6 (b).

Similarly to glassy materials induced by hard-sphere interactions, particles in the particle-rich phase of a colloidal gel also show restricted movement. However, the heterogeneous structure leads to distinct features in the dynamics. When attractions between particles are on the order of just a few $k_B T$, thermal fluctuations are strong enough to induce debonding of particles, which allows particles to explore space via diffusion and to move to a more energetically favorable morphology [83, 84, 85]. The link between the local connectivity and intermittent bonding-debonding dynamics of individual particles in colloidal gels has been quantitatively described with a microscopic model derived from experimental data, as depicted in Fig. 1.6 (c). It was shown that particles debond by thermally activated events, with a probability that decreases as the number of bonded neighbouring particles Z increases. This illustrates how the heterogeneous dynamics, characteristic for strongly disordered solids, emerge from their complex and inhomogeneous local network structure [86, 76].

While most experimental and theoretical studies have focused on colloidal

Figure 1.7: (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. Reproduced from [86] with permission from The Royal Society of Chemistry. Reprinted with permission from [86]. (b) Schematic illustrations of two stress-bearing mechanisms in a colloidal gel; stretching individual bonds and bending of gel strands. (c) Three-dimensional image of a colloidal gel reconstructed from confocal microscopy. The blue particles form the shortest chain connecting the two particles α and β (enlarged, in stripes). The second-shortest path is shown in red. Reprinted with permission from [91].

glasses [14, 75, 15, 2] and colloidal gels induced via depletion attraction [87, 88, 89, 90], local particle dynamics within mixtures, where polymers act as thickeners of the continuous phase have been almost universally overlooked in literature. Thus, the quantitative comparison between the individual particle dynamics of colloids mixed with depletants and thickeners is not clearly established, hindering the tunability of mechanical properties in such colloid polymer systems. In Chapter 2, we therefore study refractive index and density matched colloid polymer mixtures that consist of emulsion mixed with three common ‘thickeners’, which is a common term used to describe a molecule or macromolecule which increases the viscosity of the materials at the macroscopic level. We use quantitative 3D confocal microscopy to experimentally probe the microstructure and local dynamics of droplets at the individual particle level. Our results show that for polymer concentrations where the ensemble dynamics of these materials are the same, the distribution of individual particle dynamics are dissimilar and we discuss the correlation between this discrepancy and the different architectures of the added polymers.

Dynamics at the Strand Level

Colloidal gels have a hierarchical structure in which distinct structural features at clearly separable length-scales can be identified. At the microscopic scale, aggregation of the attractive particles forms gel strands, at the mesoscopic scale, gel strands connect into a percolated network structure and at the macroscopic scale the gel is considered homogeneous. Fig. 1.7 (a) shows these levels of colloidal gel structure with a confocal microscope image [92]. Besides the nature and strength of the interparticle interaction, the elastic modulus of the resultant gel depends delicately on the topology and the hierarchical structure of gels [93, 94, 95, 96, 97, 98]. In such random elastic solids, the macroscopic elasticity is attributed to a stress-bearing backbone deduced from the gel structure, as dangling ends cannot transmit stress, and thus do not contribute to the elasticity. Two modes of deformation contributing to the elasticity of the stress-bearing backbone have been proposed: bending of strands and stretching of interparticle bonds [99, 100], as depicted in Fig. 1.7 (b). Which of these modes dominates depends on the nature of the interparticle bonds. Confocal microscopy has been used to visualize the gel topology and to estimate the effective spring constant of gel strands from thermal fluctuations [101] (Fig. 1.7 (c)). These measurements showed that gels with long-ranged interactions lead to freely-rotating bonds and strands that can bend easily, so that stresses are borne mostly by stretching of interparticle bonds. By contrast, particles with short-ranged interactions resist bending, so that bending modes contribute significantly to the stress.

The strand architecture has also been shown to play an important role in the delayed collapse of colloidal gels. For gels consisting of thin strands, the delay time decreases exponentially with stress and is determined by a stress-dependent energy barrier for the rupture of interparticle bonds [102]. However, for gels with thicker strands the delay time increases by an order of magnitude, because strand rupture becomes a cooperative effect involving the simultaneous rupture of multiple bonds [103]. In simulations, space-resolved analysis of deformations and stresses of colloidal gels under shear reveals that the stretching and alignment of the gel strands induce strain hardening and that strands rupture in the regions where stresses concentrate within the network [72]. Recently, the fatigue of colloidal gels under repeated deformations has been studied by combining ex-

periments and computer simulations. A gradual softening of the network was observed with increasing strain amplitude, which was attributed to the gradual erosion of the network structure during the fatigue cycles. Simulations at single strand level suggest that this gradual weakening is a consequence of plastic deformations within individual gel strands [104]. Before rupturing, the gel strands gradually unravel due to particle rearrangements, resulting in possible strand necking and ductile failure eventually. This failure mechanism occurs regardless of the thickness and length of the strands and the range and strength of the interaction potential [105].

While strand architecture has been demonstrated to be crucial for the dynamics of colloidal gels, its role in syneresis has not been addressed. In Chapter 3, we quantify syneresis for gels consisting of solid, rubber, and liquid particles with identical average size, under the condition that adhesion of the particles to the wall is eliminated. Surprisingly, despite an universal interaction potential, we find that the largest magnitude of syneresis is observed with the gel comprising of droplets. We discuss the possible origins of this behavior in light of the contrasting modes of stress relaxation within the colloidal gel strands during syneresis. We also visualize the gel at the strand level during syneresis and find large differences in the structural rearrangements between the different systems.

Dynamics at the Macroscopic Level

Failure of colloidal solids is most often studied at the macroscopic level by rheology and imaging, on macroscopic samples such as cheese and paint. Syneresis has been studied most intensively in soft colloidal solids constituted of casein micelles, like in cheese. Casein gels have been described as a fractal structure comprising of casein clusters [106, 107]. While in most manufactured food products syneresis is considered as undesirable, it is a vital procedure during cheese production; the rennet-induced casein gel is cut into small cubes approximately 5 to 15 mm and subsequently stirred in-vat, expelling up to 90 wt% of the continuous phase containing whey. The expulsion of fluid is robustly influenced by pH and temperature [108, 109, 110] and closely relates to the external stresses applied to the network [111, 112]. Due to the weak interparticle attractions of casein micelles, the lifetime of protein bonds is affected by thermal fluctuations. Ca-

sein particles are allowed to rearrange to a state more close to the equilibrium, i.e. maximizing the contact between particles. This structural reorganisation results in inhomogeneous tensile stresses in the network. Regarding casein gel formed by skimmed milk, the ease of fluid expulsion is strongly correlated to the rearrangements of the network [108]. Rheology studies have indirectly probed this rearrangement via measurement of $\tan\delta$ which represents the ratio of the dissipated energy due to relaxation of interparticle bonds over the energy elastically stored due to distortion of the bonds [113].

Even though the pivotal role of internal stress has been recognized in governing syneresis, the studies contributing to this finding so far have centered on quantification of dimensional changes, rather than controlling the stress [114]. A common approach in studying syneresis is through accelerated measurements, such as centrifugation, which can be powerful for certain types of instabilities of food emulsions [115, 116, 117]. However, the magnitudes of the forces involved in the force balance governing syneresis are not necessarily accelerated proportionally, which may lead to different conclusions in accelerated tests compared to non-accelerated tests. In Chapter 4, we follow the syneresis of model low-fat mayonnaise, i.e. a colloid polymer mixture consisting of an oil in water emulsion with starch in the aqueous phase by long-term observation, as recent measurements on accelerated syneresis through centrifugation have proven inconsistent [114]. By systematically changing the hydrostatic pressure difference, and by considering the effect of starch on the osmotic pressure and the elasticity of the material, we investigate the driving force and the resistance that determine the rate of syneresis. We quantitatively describe syneresis in these colloid polymer mixture with a model based on Darcy's law.

To date, the investigations of macroscopic syneresis of casein colloidal gels and other soft colloidal solids are based on bulk measurements [114]. Such measurements, however, cannot provide spatial information of the material undergoing syneresis. More specifically, when a material is under stress, externally or internally, over what distance into the sample does syneresis occur and over what time scale? These questions need to be answered to describe syneresis in soft colloids from a theoretical perspective. In Chapter 5, we apply Laser Speckle Imaging measurements to both model colloidal gels and yogurt to address the

above questions by measuring spatially and temporally resolved dynamics during syneresis.

1.4 Outline

The aim of this thesis is to understand underlying physics governing syneresis in colloidal soft materials in terms of particle dynamics at multiple length scales. Below we provide a short summary for each chapter and delineate their contributions to the general aim of the thesis.

In Chapter 2, we develop a density and refractive index matched monodispersed liquid particle based colloidal system, which enables direct imaging with confocal microscopy for structure and dynamics studies. Polymers with different topology are mixed with the colloids to examine dynamics in colloid based composites. We evidence that while the static structural morphology of these composites is highly similar, these thickeners do not uniformly alter particle dynamics; by contrast, the particle level dynamics are unique to each thickener and reveal the microscopic origins of the macroscopic rheology.

In Chapter 3, we create a series of model colloidal materials to investigate syneresis with a universal interaction potential and connectivity, thus focusing solely on the composing particle. We reveal that the nature of the colloidal particle composing such materials define their magnitude of syneresis, which is highly dependent on the physical origins of stress relaxation.

In Chapter 4, we directly measure syneresis in colloid polymer mixtures like low-fat mayonnaise in a non-accelerated fashion. We address the role that the hydrostatic origins of the driving force and the resisting osmotic pressure play in syneresis. We interpret our experimental results with a model that describes the kinetics in such gravity-driven syneresis based on Darcy's law.

In Chapter 5, we apply Laser Speckle Imaging to model colloidal materials composed of particles of different nature during syneresis. So far, dynamics during syneresis have been studied without accounting for possible heterogeneities in the sample. Here, we study spatially and temporally resolved dynamics by measuring spatial maps of the dynamics during syneresis. Again, we find that the dynamics depend sensitively on the nature of the particles that form the colloidal

gel. Furthermore, this Chapter, together with Chapter 4, provides a perspective shift in investigating syneresis from conventional dimensional quantification to stress quantification.

Finally, in the General Discussion Chapter, we discuss our findings in a broader context and provide an outlook on how further development of these findings can contribute to a more integral understanding of syneresis in soft solid materials.

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CHAPTER 2

Particle Dynamics in Colloid Polymer Mixtures with Different Polymer Architecture

Nonadsorbing polymers are widely used as thickening agents for colloids. A quantitative description of the structure and dynamics of such colloid polymer mixtures is crucial to reveal the mechanisms accounting for the desired mechanical properties. In this chapter, we use confocal microscopy to study colloids with three types of commonly used polymers with different architectures: linear, subgranular cross-linked and branched microgels. All three thickeners give rise to heterogeneous colloidal dynamics, characterized by non-Gaussian displacement distributions. However, while the ensemble-averaged particle dynamics in these materials are very similar, the underlying individual particle dynamics are not. Linear polymers give rise to depletion attraction and the formation of colloidal gels, in which the majority of particles are immobilized, while a few weakly bound particles have much higher mobility. By contrast, the branched and crosslinked polymers thicken the continuous phase of the colloid, squeezing the particles into dense pockets, where the mobility is reduced and requires more cooperative rearrangements.

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2.1 Introduction

Colloids exhibit rich rheological behaviour ranging from low viscosity fluids to elastic solids, depending on the volume fraction of particles, ϕ , and the interaction between the particles [1, 2]. A soluble polymer is often added to the solvent to elicit an interaction between particles which modifies the mechanical properties, for example, by forming an elastic colloidal network at low volume fraction of particles [3]. Alternatively, incorporation of thickening polymers, such as guar and xanthan gum, can change the mechanical properties of the mixture by thickening the continuous phase, presumably without altering the interparticle interaction [4, 5]. Such colloid polymer mixtures are widely encountered in, for instance, food products, cosmetics, coatings, and drug delivery systems, where their mechanical stability determines the shelf life of the products and their performance during use [6, 7].

The resulting complex viscoelasticity of colloid polymer mixtures is intimately coupled with their microstructure and internal dynamics [8]. Therefore, quantitative descriptions of the microstructure and dynamics of such materials are crucial to reveal the mechanisms accounting for the desired mechanical properties. Most experimental [9, 10, 11], simulation [12, 13, 14, 15] and theoretical studies have focused on systems with attractive interactions between particles due to depletion attraction induced by a nonadsorbing polymer or depletion-like Morse potential. Attraction mediates the formation of sample-spanning clusters, which dynamically arrest to create a gel which is heterogeneous in local connectivity, mesoscopic structure and dynamics [16, 17, 18, 19, 20]. Such colloidal gels derive their rigidity from physically bonded particles which form strands and connecting nodes that develop into a percolating elastic network [21, 22]. Restructuring of these networks due to external or internal stresses is governed by events happening at the individual-particle level, as the bonds between the particles are typically weak; a relation between local connectivity and thermally activated dynamics at the individual-particle level has been reported recently for a depletion-induced colloidal gel [23, 24].

By contrast, local particle dynamics within mixtures, where polymers act as thickeners of the continuous phase, have received far less attention. Previous work on polymer melts containing hard nanoparticles, which have been stud-

ied extensively because of their technological importance in batteries, sensors, and implants [25], has shown that the rheological properties of such composites materials depend very sensitively on the polymer-particle and particle-particle interactions [26, 27]. Also well studied are mixtures of rigid colloidal particles with soft particles, such as microgels [28] or star polymers [29, 30]. The difference in softness between the two types of particles results in distinctly unique interactions between the components, eliciting a diverse set of states both glassy and phase-separated, intrinsically relying on the penetrability of the constituent particles [31, 32, 33].

While these studies clearly show that the dynamics in colloid polymer mixtures depend strongly on the interactions between the different components and on their relative size and softness, a quantitative comparison between particle dynamics of colloids mixed with depletants and thickeners is not clearly established, hindering the tunability of mechanical properties in such colloid polymer systems. The strong heterogeneity in particle dynamics in these systems makes a detailed direct comparison even more important, because apparent similarities at the macroscopic level may have very different microscopic origins. Clearly, such a comparative study requires detailed observations at the individual-particle level.

Additionally, nearly all studies on individual particle dynamics have been conducted on colloids containing rigid particles, while colloids comprising droplets remain largely unexplored. Not only do the droplets experience different intrinsic physics compared to rigid particles, for instance, surface mobility, deformation and coalescence, they are also ubiquitously present in food products [34, 35, 36, 37].

In this chapter, we study refractive index and density-matched colloid polymer mixtures which consist of emulsions mixed with linear polymers, subgranular cross-linked polymers, and branched microgels. We use quantitative three-dimensional (3D) confocal microscopy to experimentally probe the microstructure and local dynamics of droplets at the individual-particle level. Our results show that for polymer concentrations where the ensemble dynamics of these materials are the same, the distributions of individual particle dynamics are dissimilar. The linear polymer gives rise to depletion gels, in which most of the particles are immobilized, while few, weakly bound, particles can make large

Figure 2.1: Computer-generated renderings from experimentally determined particle positions for (a) PVP, $c_p = 8.5$ mg/ml (b) Carbopol, $c_p = 8.8$ mg/ml and (c) PAA, $c_p = 6.6$ mg/ml at a constant particle volume fraction, $\phi = 0.25$. Particles are color coded based on their coordination number, Z . Increasing shades of the corresponding colors indicate increasing Z . Scale bar in all renderings is $15 \mu\text{m}$.

excursions. By contrast, the branched and cross-linked polymers thicken the continuous phase and squeeze the particles into dense pockets, where particle mobility is characterized by caging and inter-cage hopping.

2.2 Results & Discussion

Global Structure and Dynamics

We study monodispersed colloidal copolymer droplets with radius, $a=1.0 \mu\text{m}$, made of poly(butyl acrylate)-poly(methyl acrylate) (PBA), in a solution that closely matches the density of the particles; this allows the study of the structure and dynamics of the system in the absence of gravitational stresses. The addition of a low molar fraction of poly(methyl acrylate) to the predominate PBA particles allows matching the particle refractive index to the solution, minimizing scattering and enabling 3D confocal microscopy. PBA has a low glass-transition temperature, $T_g = 220\text{K}$ and therefore exists as a viscous liquid at room temperature, so that the dispersion is an emulsion. These colloids are separately mixed with three types of polymers, a linear polyvinylpyrrolidone (PVP) K60, a subgranular cross-linked polymer (Carbopol), and a lightly cross-linked poly(acrylic acid) (PAA) polymer as microgel, resulting in three distinct colloid polymer samples all with a constant volume fraction of droplets, $\phi = 0.25$.

To begin evaluating the microstructure, we determine the coordination num-

Figure 2.2: Ensemble-averaged mean square displacements (MSD) $\langle \Delta r^2 \rangle$ of particles mixed with (a) PVP, $c_p = 0, 6.5$, and 8.5 mg/ml (b) Carbopol, $c_p = 0, 6.6, 8.8, 16.5$, and 19.8 mg/ml and (c) PAA, $c_p = 0, 4.4, 6.6, 8.8$, and 12.1 mg/ml. The ensemble-averaged MSD decrease with increasing polymer concentration. The data indicated with closed symbols in (a), (b) and (c) correspond to samples with very similar $\langle \Delta r^2 \rangle$ and are selected for a detailed comparison.

ber, Z , for each particle by identifying all of its nearest neighbors from 3D image stacks acquired with confocal fluorescence microscopy, from which the particle positions are determined using previously developed algorithms [38, 39]. Particles are identified as the nearest neighbors if their center-to-center distance is within a cutoff value, $2.2a$, with a being the particle radius. For all three polymer architectures, we observe that adding a polymer to the colloid leads to a dramatic change in the structure, from isolated particles in the absence of the polymer to a very heterogeneous structure consisting of larger clusters at high polymer concentrations, as shown in Fig. 2.1, where the deepening color shade indicates increasing Z [11]. This change in structure is also reflected in the particle dynamics, as indicated by the ensemble-averaged mean square displacement (MSD) $\langle \Delta r^2 \rangle$ shown in Fig. 2.2 as a function of lag time, τ , for three different samples. In the absence of polymers, there is a diffusive response $\langle \Delta r^2 \rangle \propto \tau$, while, unsurprisingly, for all three samples, $\langle \Delta r^2 \rangle$ decreases strongly with increasing polymer concentration.

While the structure and ensemble-averaged dynamics are very similar for the three different samples, the underlying mechanisms that lead to this behavior are quite different. The linear polymer (PVP) induces a depletion attraction between the particles due to the small polymer to particle size ratio, $\xi = R_g/a < 0.1$, where $R_g = 21$ nm is the polymer radius of gyration measured by static light scat-

tering [40]. This attraction leads to particle aggregation and the formation of a colloidal gel (Fig. 2.1 (a)), in which particle motion is strongly suppressed and becomes sub-diffusive (Fig. 2.2 (a)). For samples containing Carbopol, which consists of particles having a typical radius larger than $10\mu\text{m}$ and are athermal, there is negligible depletion attraction; yet, there is a similar heterogeneous microstructure (Fig. 2.1 (b)). This is likely due to volume exclusion by Carbopol particles, which squeeze the droplets into pockets confined between the Carbopol particles. Within each pocket, there is an increase in the local volume fraction of the droplets, which is responsible for the lower particle mobility (Fig. 2.2 (b)). Lastly, PAA consists of branched microgel-like particles and may therefore contribute to both the depletion attraction between the droplets and volume exclusion, reducing $\langle\Delta r^2\rangle$ as seen in Fig. 2.1 (c) and 2.2 (c).

Connectivity and Local Dynamics

Above, we have seen that the ensemble-averaged MSD of the three samples are very similar, even if the underlying mechanisms may be very different. However, ensemble averaging may mask the effect of local structures on the dynamics of individual particles in the mixture [24]. To further investigate this, we examine the relationship between local connectivity, i.e. Z , and individual particle dynamics for samples with very similar $\langle\Delta r^2\rangle$ for these three different polymers; specifically, the samples labeled with closed symbols in Fig. 2.2. We determine the value of $\langle\Delta r^2\rangle(Z, \tau)$ at lag time $\tau = 200\text{ s}$ for all three samples and show this as a function of Z , measured in the first frame for each time period τ , illustrated in Fig. 2.3. Here, we see a clear difference between the three samples. For the PVP sample, which forms a colloidal gel, there is a decrease of $\langle\Delta r^2\rangle(Z)$ with increasing Z ; a similar trend has been reported for colloidal gels formed by rigid particles. The observed decrease in $\langle\Delta r^2\rangle(Z)$ with increasing Z can be attributed to the fact that particles are less likely to escape from the gel strands due to thermally activated debonding events when there are more bonds per particle [24]. Surprisingly, the particle mobility in our samples is higher (by about a factor of 4) for the same Z ($Z \geq 4$) at a smaller τ , compared to the particle mobility found in colloidal gels formed by rigid particles [24], even though the attraction strength is 5 times larger in our system (Fig. 2.7 in the Appendix) and our

Figure 2.3: Particle MSD $\langle \Delta r^2 \rangle(Z)$ of particles mixed with (a) PVP, $c_p = 8.5$ mg/ml (b) Carbopol, $c_p = 8.8$ mg/ml and (c) PAA, $c_p = 6.6$ mg/ml at $\tau = 200$ s as a function of coordination number Z .

particles have a radius of $1 \mu\text{m}$ and theirs is of 700 nm . This difference might result from the difference in surface mobility between the droplets studied here and the rigid particles studied in literature. The liquid-liquid interface between droplets may, even with an attractive interaction, still be highly mobile due to sliding, which does not require bond-breaking events. By contrast, motions of a rigid particle bound to a gel strand requires the simultaneous breaking of all bonds. As a result, when having the same number of bonds, even at higher attraction strength, soft particles may still be more mobile than rigid particles. Note that in both cases, the polymer concentrations are below c^* , thus any effects of elasticity arising from the polymer concentration are negligible.

Contrary to the PVP sample which exhibits a continuous decrease in $\langle \Delta r^2 \rangle(Z)$, the Carbopol and PAA samples show a slight but continuous increase in $\langle \Delta r^2 \rangle(Z)$, with $Z = 0$ having the smallest $\langle \Delta r^2 \rangle(Z)$, Fig. 2.3 (b,c). Carbopol and PAA are cross-linked and, as a consequence, dispersions of Carbopol and PAA have a measurable elasticity at these concentrations even in the absence of particles, while the linear polymer solution is simply viscous. Indeed, we measure with rheology storage moduli $G' = 1 \text{ Pa}$ and $G' = 2 \text{ Pa}$ for Carbopol and PAA, respectively, as seen in Fig. 2.8 (b) in the Appendix. When particles are embedded in an elastic medium, the background elasticity greatly hinders particle displacements. In the Carbopol sample, in which there is negligible interparticle attraction, the particles which reside next to other particles may therefore be more mobile than the ones embedded in the elastic medium, as overcoming the background elasticity to displace costs more energy than pushing away or slid-

Figure 2.4: Time evolution of the self-part of the van Hove correlation function for particles mixed with (a) PVP, $c_p = 8.5$ mg/ml (b) Carbopol, $c_p = 8.8$ mg/ml and (c) PAA, $c_p = 6.6$ mg/ml. Decreasing shades of the corresponding colors indicate an increase in the lag time, τ .

ing next to nonbonded particles. Correspondingly, the lowest mobility is found when a particle is embedded in the Carbopol dispersion, isolated from other particles, $Z=0$, as seen in Fig. 2.3 (b). PAA can induce both attraction between particles as well as a background elasticity. We find that the behavior of the PAA sample is more similar to that of Carbopol, showing an increase in $\langle \Delta r^2 \rangle(Z)$ with increasing Z . We thus conclude that the background elasticity has a larger effect on the mobility than the depletion attraction for the PAA sample.

Step Size Distribution

Movies of each colloid polymer sample show clear heterogeneous motions. To further elucidate the microscopic dynamics at the individual-particle scale, we investigate the probability distribution of particle displacements, as characterized by the self-part of the van Hove correlation function. We consider only the x -component of the displacement and calculate the binned and normalized displacement probability distribution $P(\Delta x, \tau)$ by measuring the displacement $\Delta x(\tau)$ for each tracked particle. These distributions are shown for three different samples for different lag times in Fig. 2.4; as seen in the symmetry of the distributions, the preshear and loading into sample chambers did not align or orient the sample microstructure. For all three types of polymers, we observe significant deviations from the Gaussian distribution expected for the Brownian motion. All distributions exhibit exponential tails, in addition to a central Gaussian region. Previous studies have shown that such non-Gaussian behavior is due to

Figure 2.5: (a) Width of the Gaussian distribution σ (b) fraction of hopping particles A_{ex} , and (c) decay length of the exponential tail, λ , for (green) PVP, $c_p = 8.5$ mg/ml, (orange) Carbopol, $c_p = 8.8$ mg/ml and (blue) PAA, $c_p = 6.6$ mg/ml as a function of lag time, τ .

strongly heterogeneous particle dynamics, which can be qualitatively described as the superposition of two families of particles: localized particles, performing rattling motions around their initial positions, contributing to the Gaussian central part, and mobilized particles, performing sporadic larger displacements, or hops, leading to exponential tails [41, 42].

We further analyze these data by extracting the width σ of the central Gaussian region, the decay length λ of the exponential tail, and the relative amplitudes of the two populations. We do this by fitting a Gaussian $P_G(\Delta x) = (A_G/\sqrt{2\pi\sigma}) \exp(-\Delta x^2/2\sigma^2)$ to the central region ($|\Delta x| < 0.3\mu\text{m}$) and an exponential function $P_{ex}(\Delta x) = \frac{1}{2}A_{ex}\lambda \exp(-|\Delta x|/\lambda)$ to the tail region ($|\Delta x| > 0.6\mu\text{m}$). An exemplary fit is depicted in Fig. 2.9 in the Appendix. Here, A_G and A_{ex} denote the amplitudes of the Gaussian and exponential regions, which correspond to the fraction of localized and hopping particles, respectively.

In all three samples, the width of the Gaussian region σ remains small and increases only slightly at very large τ (Fig. 2.5 (a)). This indicates that the particles belonging to this population are rattling around their average position and cannot move far. We note that the free self-diffusion time of these particles, $\tau_B \approx 3\pi\eta a^3/k_B T$ is on the order of 1 s, so that our data do not show the initial diffusive region expected for shorter times. The population belonging to the exponential tails, by contrast, shows a clear difference between the PVP sample, on the one hand, and the Carbopol and PAA samples on the other: in the PVP sample, A_{ex} is much smaller than in the other samples (Fig. 2.5 (b)), while λ is

much larger (Fig. 2.5 (c)). This indicates that this sample contains much fewer mobilized particles than the other two, but the typical distance that these mobilized particles move is much larger. This is likely related to the difference in the structure between the samples as the PVP sample is a colloidal gel and particles must detach from gel strands before they displace. Due to the attraction strength, $U \sim 7 k_B T$, such debonding events are relatively rare, leading to a small population of mobile particles. However, the particles that do escape can explore different configurations in the gel before they reattach in a different location, so that the distance that they can travel is relatively large. By contrast, in the other two samples, the particles are confined to the interstitial spaces between the polymer particles, but there is negligible or much weaker attraction between the particles. The slow-down of the dynamics in this case is mostly due to an increase in the local volume fraction, and may be compared with the dynamics in concentrated colloidal suspensions approaching a glass transition [43, 44, 45]. It is well-established that the dynamics in such systems is characterized by short-time rattling of particles within the cages formed by neighboring particles and occasional cage rearrangements, which involve a cooperative motion of multiple particles. These cage-breaking events give rise to dynamic heterogeneity and the non-Gaussian tails observed in the van Hove function [44]. Apparently, these cage rearrangements occur more frequently than the debonding events in the colloidal gel sample. Yet, because of the high local particle volume fraction, they are limited in spatial extent, so that the typical distance, λ , moved by the mobile particles in these samples is smaller than that in the colloidal gel, as seen in Fig. 2.5 (c).

These observations furthermore suggest that the samples with PAA microgels behave more like the Carbopol samples rather than like the PVP samples, indicative of the dominant effect of PAA is volume exclusion, rather than a depletion attraction. However, upon closer inspection, we do observe some differences between the PAA and Carbopol samples: in the PAA samples, the width of the Gaussian region gradually increases at large τ , see Fig. 2.4 (c) and Fig. 2.5 (a), suggesting that the confinement in these samples is less severe than in the Carbopol samples. Moreover, the fraction of mobile particles increases as a function of τ in the PAA sample, while in the Carbopol sample, it remains more or less

Figure 2.6: Schematic illustration of colloid polymer mixtures structure with PVP (green), Carbopol (orange) and PAA (blue).

constant; this again implies a weaker confinement, as seen in Fig. 2.5 (b).

2.3 Conclusion

Our results demonstrate the necessity of dynamics at the individual-particle level in distinguishing materials consisting of colloids mixed with various architectures of polymers, which would help to elucidate the origin of tunable viscoelastic behavior in such materials. In a colloidal gel, the dynamics are characterized by a large majority of immobilized particles and a small fraction of weakly bound particles that can make large excursions. By contrast, colloids that are thickened by subgranular polymer gel particles lead to dense pockets of particles characterized by heterogeneous dynamics reminiscent of concentrated colloidal suspensions or glasses (Fig. 2.6). These microscopic differences could manifest macroscopically, for example, in how the materials age and coarsen, or in the long-term stability of products against syneresis or delayed failure. We hope to stimulate future theoretical efforts in understanding the interplay between particle dynamics and the complex rheological response in such colloidal composites. Additionally, the dependence of particle nature, rigid particle or droplet, on particle dynamics calls for interesting studies toward a complete description.

2.4 Materials & Methods

Colloid Polymer System

All chemicals are purchased from Sigma Aldrich unless otherwise specified. We fabricate colloid polymer mixtures consisting of poly(butyl acrylate–methyl acrylate) (PBA) particles, mixed with polyvinylpyrrolidone (PVP) K60 or with poly(acrylic acid) (PAA) with two different architectures. PVP is chosen for these experiments to ensure a linear polymeric topology as the synthesis of poly(acrylic acid) often leads to undesired branching and other side reactions during radical polymerization [46, 47, 48, 49]. Monodispersed PBA-MA particles, sterically stabilized by PVP K30, are synthesized according to a published method with modification [50]. The recipe for seed particles by dispersion polymerization at 70 °C is as follows: a monomer mixture containing butyl acrylate and methyl acrylate with a ratio of 70/30 (v/v %); PVP K30 as a dispersant with 20 vol% of monomers; 4,4'-azobis-(4-cyanopentanoic acid) as an initiator at 1 wt% to total monomer; and a solvent medium comprising methanol and H₂O with a ratio of 88/12 (v/v %). PBA has a low glass-transition temperature (T_g) and thus exists as a liquid at room temperature. The droplets have a radius, $a = 1.0\mu\text{m}$, and a polydispersity of $\sim 5\%$, as determined by optical microscopy and dynamic light scattering. The droplets are dispersed at a volume fraction $\phi = 0.25$ in the medium of dimethyl sulfoxide (DMSO) and H₂O. This solvent mixture confers the ability to tune the solvent ratio to simultaneously match the refractive index and the density with that of the PBA-MA droplets [51]. A ratio of 95/5 (v/v %) of DMSO and H₂O is chosen for the current study with 3 mM NaCl to screen charge interactions. Droplets did not settle to any observable extent after centrifuging at 1200g for 19 h, confirming the neutral buoyancy of the samples. Optical clarity permits the samples to be observed with a confocal microscope approximately 100 μm into the sample without losing contrast. Sulfo-cyanine3-carboxylic acid (Lumiprobe) is dissolved in the continuous phase to enable fluorescence imaging through excitation by a 532 nm laser. PVP K60 has a molecular weight of 360,000 g/mol with a radius of gyration $R_g = 21\text{nm}$ [40] and an estimated $c^* = 3M_w/4\pi R_g^3 N_A = 15.4\text{ mg/ml}$. The two different topologies of PAA are lightly cross-linked PAA (Mw = 1,250,000 g/mol) and Carbopol (Ultrez

U10, Lubrizol) which is cross-linked PAA at the subgranular length scale. This allows us to have different size ratios between the droplets and polymers. A more detailed characterization of the added polymers is given in Table 2.1 in the Appendix, where the average size and the overlap concentration of the polymers are given. We also show a rheological characterization of the PAA and carbopol samples, both with and without particles, in Fig. 2.8 (a) and Fig. 2.8 (b) in the Appendix. We define the volume concentration of the polymer as the mass of polymer, in milligrams, divided by the volume of the solvent, in milliliters. A range of concentrations of added polymers are investigated. Stock solutions of the colloids and the polymers are prepared separately and are used after a waiting period of at least 24 h to allow equilibration with the solvent mixture. Mixing of the samples is done by tumbling on a rotating wheel for 24 h.

Confocal Microscopy and Image Processing Analysis

Sample chambers are made of two rectangular cover slips (21×26 mm) glued to a standard glass microscope slide with a few mm 2D channel in-between. The sample area is approximately $5 \text{ mm} \times 25 \text{ mm}$. A 3D channel is created by placing a third circular microscope cover glass (diameter = 50 mm) on top with more glue. The empty chamber is exposed to ultraviolet light for the glue (Norland 61 NOA) to cure. The mixture of colloids and polymers is pipetted into the sample chamber, which is subsequently sealed using a two-component epoxy glue. Three-dimensional images are collected using a high-speed confocal microscope with a micro-lens array (VisiTech VT-Infinity3) and a silicon oil immersion objective (Nikon). The depth of the focal plane, z , is controlled by a piezo-element mounted on the microscope nosepiece. Images are captured at 780 or 1000 frames per second, with 256×256 pixels of size of $0.28 \mu\text{m}$ in both the x - and y -directions. Each 3D image stack typically contains approximately 200 images, each offset by $0.2 \mu\text{m}$ in the z -direction. One thousand stacks are obtained for all samples. Wall effects are avoided by capturing images at least $10 \mu\text{m}$ away from the cover glass. Fluorescence is excited using a 532 nm DPSS laser; the fluorescence is filtered with a 560 nm long-pass filter and is detected with a Hamamatsu OCRA II CCD camera.

The intensity of the acquired images is inverted so that the particle-rich

phase appears bright and the particle-poor phase appears dark. First, a spatial band-pass filter is applied to the images to eliminate long-wavelength contrast gradients and short-wavelength pixel-to-pixel noise. Then, the Cartesian center of each droplet is located for each image stack with a previously developed algorithm [38, 39]. Based on the coordinates of the droplets, the quantitative 3D microstructure of the droplets can be rendered with a ray-tracing software (Blender). The coordination number for each droplet is determined by identifying all of its nearest neighbors. Droplets are identified as the nearest neighbors if their center-to-center distance is within a cutoff value, $2.2a$. Once the coordinates have been found in each image stack, trajectories of droplets can be calculated, describing the droplet motion [38, 39]. The magnitude and the direction of the ensemble-averaged affine drift are computed after particles have been tracked. We then update particle locations by removing this drift, from which refined particle trajectories are calculated. We note that the drift is still apparent at larger τ ; data at lag times for which the slope of the MSD versus τ is higher than 1, indicating drift, has been disregarded.

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Appendix

Attraction Strength

The PVP induces a depletion attraction between the colloidal particles. The depth of the attractive minimum induced upon adding PVP can be estimated as

$$\frac{U(r)}{K_B T} = \Pi(c) V_{\text{overlap}} \quad (2.1)$$

where $\Pi(c)$ is the osmotic pressure of the polymer in solution, and V_{overlap} is the overlap volume of the depletion zones around the particles as a function of r , the inter-particle separation. The V_{overlap} can be determined by purely geometric

Figure 2.7: Calculated depletion potential for PVP sample (circle) and polystyrene sample (diamond) as a function of depletant concentration.

considerations: [9]

$$V_{\text{overlap}} = \frac{\pi}{6} \sigma^3 (1 + \xi)^3 \left(1 - \frac{1.5r}{\sigma(1 + \xi)} + \frac{0.5r^3}{\sigma^3(1 + \xi)^3} \right) \quad (2.2)$$

Here $\sigma = 2a$ is the diameter of the colloidal particles and $\xi = R_g/a$ is the size ratio between polymer and particle. The osmotic pressure $\Pi(c)$ can be estimated by integrating the analytical form of the osmotic modulus as a function of concentration using the Oota-Ohno expression, [52, 53]

$$\frac{M_w}{RT} \frac{d\Pi}{dc} = 1 + \frac{1}{8} \left(9X - 2 + \frac{2\ln(1+X)}{X} \right) \exp \left(\frac{1}{4} \left(\frac{1}{X} + \left(1 - \frac{1}{X^2} \right) \ln(1+X) \right) \right) \quad (2.3)$$

where X is the reduced polymer concentration given by $X = (16/9)c/c^*$, with c^* representing the overlap concentration of the polymer. At a [PVP] = 8.5 mg/ml, the attraction strength between droplets is approximately $7 k_B T$. Based on the information provided in [24], using Eq. 2.1, 2.2 and 2.3 the calculated attraction strength between rigid particles is approximately $1.4 k_B T$, as shown in Fig. 2.7.

Figure 2.8: (a) Storage moduli as a function of frequency for 8.8 mg/ml Carbopol (red) and PAA (blue) polymers; open symbols represent polymer only and closed symbols represent mixed with particles at $\phi = 0.25$. (b) Storage moduli as a function of added polymer concentration for Carbopol (red) and PAA (blue).

Rheology Measurement

Rheology measurements are performed on a stress-controlled rheometer (Anton Paar MCR 501) in a cone-plate geometry, which has a sample volume of 0.57 ml and a cone with a radius of 50 mm. In the frequency sweep, a frequency from 100 Hz to 0.0001 Hz is applied at a strain of 0.1%. In the strain sweep, a strain from 0.01 % to 100 % is applied at a frequency of 1 Hz. In all cases, a solvent trap is used to prevent solvent evaporation. All suspensions are rejuvenated by shearing (shear rate = 1 s^{-1}) for 5 min and left to relax for 50 min before commencing the measurement.

Storage moduli as a function of frequency for 8.8 mg/ml PAA and Carbopol sample without and with PBA particles at $\phi = 0.25$ are shown in Fig. 2.8 (a). Inclusion of the colloids slightly increases the elasticity of the measured samples. At the polymer concentration discussed in Fig. 2.3, the composite comprising PVP, the linear polymer, has a storage modulus too low to be measured with the rheometer. Storage moduli as a function of added polymer concentration for Carbopol and PAA are demonstrated in Fig. 2.8 (b), from which the overlap concentration of PAA and Carbopol can be estimated as the first concentration where G' is measurable. The storage moduli are obtained from the linear re-

gime in a strain sweep measurement. No data for PVP is included here due to the elasticity of a linear polymer solution being too small to measure at these concentrations which are all well below the entanglement concentration for this molecular weight PVP.

Characterization of the Added Polymer

Characterization of the added polymers is listed in Table. 2.1. In terms of average size, the PVP data is obtained from literature [40]. Microgel data is measured by DLS at a concentration, 1.1 mg/ml, well below c^* , as shown in Fig. 2.8 (b). Carbopol data is estimated from our 2D confocal microscopy images. Values of c^* have also been included in this table according to Fig. 2.8 (b).

Polymer	PVP	PAA	Carbopol
Average Size	21 nm (R_g)	240 nm (R_d)	25 μm (diameter)
c^* (overlap, mg/ml)	15.4	6.6	8.8

Table 2.1: Characterization of the added polymer on average size and overlapping concentration.

Step Size Distribution

An example of Gaussian fit and the exponential fit for the step size distribution is shown in Fig. 2.9.

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Figure 2.9: Example of a fit (---) to the self part of the van Hove correlation function in different regions (●): Gaussian fit for $|\Delta x| < 0.3 \mu\text{m}$ and the exponential fit for $|\Delta x| > 0.6 \mu\text{m}$.

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CHAPTER 3

Syneresis of Colloidal Gels: Endogenous Stress and Interfacial Mobility Drive Compaction

Colloidal gels may experience syneresis, an increase in volume fraction through expulsion of continuous phase. This poroelastic process occurs when adhesion to the container is weak compared to endogenous stresses which develop during gelation. In this chapter, we measure the magnitude of syneresis, $\Delta V/V_0$ for gels composed of solid, rubber, and liquid particles. Surprisingly, despite a constant thermoresponsive interparticle potential, gels composed of liquid and elastic particles synerese to a far greater extent. We conclude that this magnitude difference arises from contrasting modes of stress relaxation within the colloidal gel during syneresis either by bending or stretching of interparticle bonds.

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3.1 Introduction

When colloidal particles in a dispersion are made attractive, they aggregate into fractal clusters which, even at low volume fraction, ϕ , grow to form a space-spanning network, or gel. These gels determine the rheological behavior of many consumer products; their shelf-life relies on the mechanical stability of the colloidal gel network which acts as scaffold to provide rigidity to the material. Understanding the mechanical stability of such colloidal gels is thus of crucial importance for controlling the properties of many soft solids. Once a colloidal gel forms, the heterogeneous structure, often bonded through weak non-covalent interactions, is immediately subject to body forces such as gravity [1], surface forces such as adhesion to container walls [2, 3] and shear forces[4]; the delicate balance between these forces acting on the system as a whole determines its fate. Interestingly, even in the absence of external stresses, colloidal gels undergo slow internal rearrangements that cause the network structure to either gradually age and coarsen [5, 6] or densify by a mechanical instability known as syneresis [7, 8, 2, 9], which is a compaction of the gel accompanied by the expulsion of the continuous phase. While mechanical failure of colloidal gels subjected to external stresses, both shear or gravitational, has been studied in detail, there is a dearth of studies on catastrophic failure of gels due to internal stresses that accumulate during the formation of the gel. Furthermore, few studies have investigated colloidal gels formed by particles other than solid spheres, while most colloid-based consumer products are comprised of soft particles; interestingly, these products nearly universally exhibit syneresis. As a result, predicting the stability of colloidal gels remains prohibitively difficult as the interplay between internal stress, nature of particles, and adhesion to the solid container surfaces is not yet established.

In this chapter, we investigate the failure of colloidal gels due to syneresis driven by internal stresses and in the absence of any external stresses such as adhesion to the container walls and gravity. We find that syneresis is a poroelastic and reversible phenomenon; when the attractive forces are removed, the collapsed gel relaxes back to a fluid dispersion of particles, indicating that neither coalescence nor irreversible aggregation occurs. Furthermore, we find that the normalized magnitude of syneresis, $(V - V_0)/V_0$, with V and V_0 the final and ini-

Figure 3.1: Schematic illustration of the model systems

tial volume, respectively, is highly dependent on the particle nature; colloidal gels composed of soft particles, such as liquid droplets and elastic rubber particles, display larger ΔV than gels formed of solid particles with the same interparticle attraction. In all cases, syneresis arrests before maximum compaction is reached, which we relate to the elastic stresses that develop during syneresis which cannot relax by particle rearrangements or connectivity changes in these strongly attractive gels.

3.2 Results & Discussion

To minimize external stresses on these colloidal gels, we prepare a dispersion of polystyrene particles of radius, $r = 275$ nm, at $\phi=0.01$ in a density matched solution of 100 mM NaCl, 55/45 vol% D_2O/H_2O [10]. To this dispersion, 0.1wt% of a thermoresponsive surfactant is added which adsorbs onto the particle surface and induces a reversible temperature-triggered attractive force between the particles when heated above $32^\circ C$ [11]. The dispersion is heated to $45^\circ C$ in a spherical glass geometry. Upon heating, the particles become attractive, with an attractive strength, $U \gg 50k_B T$ [12, 11] and an elastic network forms. Im-

Figure 3.2: (a–d) Image sequence of syneresis in a spherical geometry for a thermoresponsive solid polystyrene particle dispersion at $\phi_0 = 0.01$ heated to 45°C . (e) Kinetics of syneresis in a polystyrene particle dispersion at $\phi_0 = 0.01$; solid red line is a fit to an exponential function. Inset: characteristic syneresis time, showing $\tau \sim \phi_0^{-1}$.

mediately after formation, the network begins to contract, expelling the continuous fluid, as illustrated in Fig. 3.1. We macroscopically image this syneresis process over time, as shown in Fig. 3.2 (a–d). Crucially, the container walls are treated with a polyelectrolyte multilayer; this surface coating prevents the colloidal particles and surfactant from adhering and adsorbing to the surface of the

container [13]. By contrast, if the boundary of the spherical sample cell is adhesive to the surfactant, the gel forms and remains stable with the contraction balanced by adhesion to the rigid container walls. Nearly all experimental studies on the mechanical failure of colloidal gels do not control adhesion; syneresis having been observed only after the container is rotated, breaking adhesive bonds to the walls [2] or by traditional means through knifing of cheese curd [7]. By forming the gel network *in situ* in all experiments, endogenous contractile tension is generated by the gel network, as no shear is exerted on the network by mixing or pipetting, which is known to directly affect the gel network connectivity [14], anisotropy [15], and failure [4].

To quantify the syneresis process, we calculate the normalized change in volume fraction with time, $(\phi(t) - \phi_0)/\Delta\phi$ by extracting the projected area occupied by the gel from the images as shown in Fig. 3.2 (a-d). As the gel contracts, ϕ reaches a plateau within several hours, as seen in Fig. 3.2 (e). The kinetics of the process can be described accurately with an exponential function

$$\frac{\phi(t) - \phi_0}{\Delta\phi} = 1 - \exp(-t/\tau)$$

with a characteristic time scale τ that decreases with increasing initial volume fraction as $\tau \sim \phi_0^{-1}$, as illustrated in the inset of Fig. 3.2. These observations resemble the compaction of colloidal gels under the influence of external stresses, such as gravity, which has been described successfully as a poroelastic relaxation process with a rate that is limited by the fluid flow through the elastic porous material [1, 8].

The characteristic timescale of such a poroelastic process is given by $\tau \sim \frac{\eta(1-\phi_0)R^2}{k_0K}$ with η the viscosity of the continuous phase, R the initial size of the material, which in the present case corresponds to the radius of the contracting sphere, K the bulk modulus of the gel, and k_0 the permeability of the gel network. For small initial volume fractions $\phi_0 \ll 1$, we thus expect $\tau \sim 1/k_0K$. Rather than the typically used Kozeny-Carman equation, the permeability of a colloidal gel network has been shown to scale as $k_0 \sim \frac{a^2}{\phi_0^{2/(3-d_f)}}$, where a is the radius of the particle and d_f is the fractal dimension [1]. For the present case of strongly attractive particles, we expect close to diffusion-limited aggregation,

leading to $d_f \approx 1.9 \pm 0.1$, thus $k_0 \sim \phi_0^{-1.8}$ [16]. Our observation that $\tau \sim \phi_0^{-1}$ suggests that $K \sim \phi_0^{2.8}$, which corresponds well to previous work on the compression of colloidal aggregates [17], and which, interestingly, is also of similar scaling observed for the shear modulus, $G'(\phi_0)$, discussed below. Implying that $K/G \sim \mathcal{O}(1)$, which has not been thoroughly investigated [17].

Most food products that exhibit syneresis consist of gels composed of droplets while most experimental studies on gel dynamics consist of solid particles, similar to the polystyrene particles. To explore the effect of particle nature on the extent of syneresis, we use emulsion polymerization to synthesize monodispersed viscous droplets with the same radius, $r=275\text{nm}$, composed of polybutylacrylate, a low glass transition temperature polymer. Additionally, we prepare cross-linked rubber polybutylacrylate particles which are deformable and elastic, by adding a crosslinker, ethylene glycol diacrylate, at 0.7mol% during the emulsion polymerization. We adsorb the same surfactant at the same concentration onto these particles as used previously, thus maintaining a near constant interparticle attraction for all three different systems (Fig. 3.1).

After heating, all colloidal gels exhibit arrest after an initial syneresis reaching a final volume fraction, ϕ_f , which is less than ϕ_m , the maximum possible volume fraction. To elucidate if the arrest that occurs is a stationary state, or results from kinetically arrested configuration, we perform cycling experiments: each sample is heated, permitted to undergo syneresis until arrest, after which the expelled fluid is removed, and the sample is cooled to 25°C. Cooling the sample removes the interparticle attractive potential, causing particle dissociation within the colloidal gel, resulting in a fluid dispersion with a now higher volume fraction $\phi_0 + \Delta\phi$. In all cases, $\langle r \rangle$ as measured using dynamic light scattering, remains constant for all cycles; emphasizing the lack of coalescence or irreversible aggregation during syneresis. As the dispersion is heated again, the gel synereses again and additional fluid is expelled; the process is repeated N_c times and $\phi(N_c)$ determined gravimetrically after the end of each cycle, as shown in Fig. 3.3. In all three colloidal gels, the observed positive $\Delta\phi(N_c)$ indicates a kinetically arrested configuration during the previous cycle; when internal stresses are released upon cooling, particles are free to find more favorable configurations when attraction is induced again in the next cycle. The droplets and rub-

Figure 3.3: Cyclic syneresis in colloidal gels with volume fraction, ϕ , taken after each syneresis cycle for, solid particle (diamond), rubber particle (square), and droplets (circle). Error bars represent standard deviation ($N=2$).

ber particles have a nearly identical volume fraction increase for $N_c=1$ but deviate at higher N_c , reaching different plateau values; the final cycle packing fraction is $\phi=0.82$ and $\phi=0.51$ for the droplets and rubber particle gels, respectively. This difference can be attributed to the higher deformability of droplets. Rubber particles resist deformation with elasticity originating from covalent bonds within the polymer network, while droplets only resist by Laplace pressure. This droplet final volume fraction, $\phi_m = 0.82$, is higher than $\phi(\text{hcp}) = 0.747$, which requires significant droplet deformation [18]. Clearly distinct from droplets and rubber particles, solid particles exhibit a slowly increasing $\phi(N_c)$ which remains well below $\phi(\text{rcp}) = 0.64$ during these cycling experiments. The origin of this difference must lie with how these particles respond to the emerging endogeneous stress during gelation and subsequent syneresis.

To further explore this difference, all three dispersions for different ϕ_0 are heated to 45°C ; all samples exhibit syneresis of varying magnitude. This mag-

Figure 3.4: Magnitude of syneresis, $\Delta V/V_0$, for solid particles (diamond), rubber particles (square), and droplets (circle) as a function of scaled initial volume fraction, ϕ_0/ϕ_m . Error bars represent standard deviation ($N=2$).

nitude is quantified by the normalized volume change, $\Delta V/V_0$ at steady state, after 4 hours, as shown in Fig. 3.4. For solid particles, $\Delta V/V_0$ decreases approximately as $(\phi_0/\phi_m)^{-1.2}$. By contrast, for both droplets and rubber particles $\Delta V/V_0$ remains nearly constant for $\phi_0/\phi_m < 0.3$, then rapidly approaches as $\phi_0/\phi_m \rightarrow 1$; emphasizing a nearly universal syneresis mechanism between these two particle dispersions. This difference must again originate in the stress relaxation modes during syneresis, a consequence of how the colloidal gel structure bears stress. In the absence of syneresis, an elastic gel network forms which bears stress by either bending of strands or stretching of individual interparticle bonds leading to an increase in the center to center distance between particles [19, 20]. For pair-wise particle interactions, centrosymmetric interparticle po-

tentials such as polymeric depletion or this surfactant induced attraction, the free energy cost of relative particle rotation and, therefore bending, is near zero, leading to stress being born only by stretching interparticle bonds. However, once the cross-section of each gel strand becomes more than one particle, bearing stress by bending energy may become appreciable [19]. The scaling of $G'(\phi)$ provides a measurement of how the gel bears any applied stress [21, 20]. In a rheometer, we form gels by heating dispersions and measure $G'(\phi)$ as shown in Fig. 3.5 (a); syneresis is eliminated due to adhesive walls. For $G' \sim (\phi)^\nu$, a small exponent value of $\nu = 1.7$ indicates gels bearing stress by stretching interparticle bonds; while a higher exponent, $\nu = 3.3$, indicates gels bearing stress by bending network strands [22, 23, 24]. Both mechanisms are not exclusive with the measured scaling exponents often lying between these two extremes. Based on ν shown in Fig. 3.5 (a), droplet and rubber gels bear stress by stretching predominately, while stress bearing in the solid gels is dominated by bending. Crucially, surfaces of both droplets and rubber particles are fluid and smooth, permitting lateral surfactant diffusion. This surface mobility likely permits these 'soft' particles to exhibit kinetic arrest only after obtaining a higher ΔV . Due to the surface mobility, individual particles slide relative to one another with near zero free energy cost, therefore gels comprising of soft particles can only bear stress by stretching. By contrast, solid particle gels bear stress by bending and arrest at a lower volume fraction due to surface asperities and a lack of surface mobility, as illustrated in shown in Fig. 3.5 (b).

Again we observe two contrasting dependencies between colloidal gels formed of solid particles and those comprising of droplet and rubber particles, in addition to this, same dependence already being observed in syneresis magnitude, i.e. Fig. 3.4. To explain this contrast, we hypothesize that there is an initial syneresis pressure, $P \sim \phi_0^2$; this is in analogy to the second virial approximation for the osmotic pressure of non-ideal dispersions, which scales as $\Pi \sim B_2\phi^2$, with the second virial coefficient, B_2 , being negative here as particles attract forming additional bonds [25]. This negative pressure leads to a compression of the material which is counteracted by network elasticity. Combining, K being defined as $\Delta V/V_0 = -P/K$, and our previous result which implies $K \sim G \sim (\phi)^\nu$, then for solid particles with $\nu = 3.2$ suggests $\Delta V/V_0 \sim \phi_0^{2-3.2} \rightarrow \phi_0^{-1.2}$ in

Figure 3.5: (a) Storage moduli, G' , of colloidal gels for solid particles (diamond), rubber particles (square), and droplets (circle) as a function of volume fraction, ϕ . (b) Schematic illustration of contrasting modes of stress relaxation between droplet and solid particles.

agreement with syneresis results seen in Fig. 3.4. Similarly, for droplet and rubber particles, $\nu \sim 2$ suggests $\Delta V/V_0 \sim \phi_0^{2-2} \rightarrow \phi_0^0$ also in concert with Fig. 3.4. For larger ϕ_0/ϕ_m there is a strong deviation from this simple scaling, as $\Delta V/V_0$ approaches zero, likely due to B_2 being no longer pair-wise additive. This scaling assumes that syneresis is counteracted by network elasticity, thus, arrest in droplet and rubber gels is likely a consequence of network connectivity: The gel contracts until further contraction would require the breaking of interparticle bonds which is energetically unlikely as the attractive strength, is $\gg 50k_B T$ [12, 11].

To directly illustrate these arrest modes, syneresis is observed at the microscopic level by heating quasi-2D disks of gels within non-adhesive microfluidic chambers consisting of droplets ($\phi_0 = 0.05$) and solid ($\phi_0 = 0.02$) particles such that $G'(\phi_0)$ is comparable; the low half of these disks are shown in Fig. 3.6 (a-d), time-lapse images from the recorded syneresis movies. The onset of syneresis is defined as the initial detachment from the chamber wall, $t_d = t = 0$ s; Fig. 3.6 (a,c) are immediately after t_d . Particle Image Velocimetry (PIV) analysis at $t = 10$ s indicates displacements are directionally disorganized in both cases. Interestingly, at $t=130$ s, displacement vectors in the droplet gel appear radially oriented, while disordered displacements for the solid gel persist, as seen in Fig.

Figure 3.6: Quasi-2D gels consisting of droplets (orange), $\phi_0=0.05$, at (a) $t=10$ s and (b) $t = 130$ s, of solid particles (blue), $\phi_0=0.02$, at (c) $t = 10$ s and (d) $t = 130$ s. Green vectors represent the velocity over 5 s; vectors are enlarged 1.5 times and 3 times in the gel consisting of droplet and solid particles, respectively. (e) Standard deviation of vorticity normalized by average magnitude of vector, σ/μ , for droplets (circle) and solid particles (diamond) as a function of time.

3.6 (b) and (d) respectively. To quantify this difference, the spatially averaged vorticity is computed using PIV for an interrogation window, and its standard deviation, σ , is normalized by the averaged velocity, μ ; the quantity, $\sigma(t)/\mu(t)$ is shown in Fig. 3.6 (e). A lower $\sigma(t)/\mu(t)$ is indicative of a uniform vorticity or arrest, while, a large $\sigma(t)/\mu(t)$, is indicative of a spatial inhomogeneity of the vorticity possibly arising from non-affine motions.

As shown in the syneresis movies, both gels experience a pore size increase for $t < 0$, a process of local syneresis leading to an increasing number of interparticle bonds. However, only for the droplet gel is this clearly followed by a macroscopic radial movement of gel strands. These two processes are concomitant; a large $\sigma(t)/\mu(t)$ corresponds to pore size increase and non-radial displacement, while radial bulk syneresis drives $\sigma(t)/\mu(t) \rightarrow 0$. Conversely, for the solid gel at $t > 0$, no clear radial motion is observed, resulting in a large $\sigma(t)/\mu(t)$ persisting, only decaying slowly to 0 during arrest, as seen in Fig. 3.6 (e). As these two different gels have similar $G'(\phi_0)$, see Fig. 3.5 (a), this difference must originate in contrasting surface mobility. Both a decreasing pore size and radial movement imply a nearly affine deformation, similar to what has been shown for networks of beams with low bending modulus [26], as is the case for the droplet gel with permitted interparticle sliding. By contrast, the non-radial, non-affine motion of the solid gel with a lack of interparticle sliding, i.e. higher bending modulus, results in a lingering $\sigma(t)/\mu(t) > 0$ before arresting at approximately $t \sim 500$ s.

3.3 Conclusion

We have shown that colloidal gels undergo syneresis when the adhesive boundary conditions are eliminated and the gel forms *in situ*. Interestingly, we observe that the magnitude of syneresis, $\Delta V/V_0$, is highly dependent on the surface mobility and local deformability of the particle composing the gel; these two properties are nearly universally overlooked in colloidal materials, yet, they likely play key roles in rheologic responses, especially during mechanical breakdown [27]. While syneresis is more readily seen in 'soft' particle gels, especially foods, we have shown that it is still not negligible in gels composed of solid particles, but often not observed experimentally due to adhesive container walls. However, this does not preclude local syneresis within the network which may be interpreted as aging in literature [6, 28, 29].

3.4 Materials & Methods

Sample Preparation

Poly(N-isopropylacrylamide)(pNIPAM) surfactant is synthesized to a published method [11]. Polystyrene particles of $\langle 275 \rangle$ nm radius are synthesized using dispersion polymerisation of styrene (Sigma) at 80°C for 2 hours using AIBN (Sigma) as a radical initiator [10]. The dispersion is filtered and washed by centrifugation (3x) into 0.1 wt% pNIPAM surfactant and 100 mM NaCl solution to a final $\phi=0.2$. The recipe for polybutylacrylate (PBA) droplets by UV initiated emulsion polymerization is as follows: a disperse phase, comprising of butyl acrylate with 0.3 wt% 2,2-Dimethoxy-2-phenylacetophenone as photoinitiator, and a continuous phase, comprising of 3 mM NaCl and 0.1 wt% pNIPAM, are mixed with a ratio 1/4 (v/v%). The mixture is vortexed and then bath-sonicated at 10°C for 25 min. After bubbling with N_2 for 10 min in a sealed vial, the mixture is exposed to UV light for 10 min while gently mixing at 10°C. The mixture is left overnight for complete polymerization at room temperature. PBA has a low glass transition temperature (T_g) and thus exists as liquid at room temperature. The particles have an average radius, $\langle r \rangle=275$ nm, as determined dynamic light scattering; multiple batches were produced until the diameters matched

between both polystyrene and PBA particles. The rubber particles are prepared in a similar fashion as PBA droplets. The only difference is that ethylene glycol diacrylate at 1 vol% (0.7 mol%) of the monomer is added to the disperse phase before mixing for cross-linking purpose. Both PBA droplets and rubber particles are filtrated and dialyzed against 0.1 wt% pNIPAM surfactant and 100 mM NaCl solution to a final $\phi=0.4$ approximately.

PEM coating is prepared as the following procedure according to [13]: Solutions of 1 wt% cationic polymer, polydiallyldimethylammonium chloride (M_w 400k-500k, Sigma), in 1M NaCl and 1wt% anionic polymer, sodium polystyrene sulfonate ($M_w \sim 200$ k, Sigma) in 1M NaCl are prepared. The solutions are filtered with $0.45 \mu\text{m}$ hydrophilic filter. To begin the process, the glass container is cleaned using a plasma cleaner. This makes the glass anionic, negatively charged. The cationic polymer solution is first added to the container and then rinsed away with sufficient amount of deionized water by filling the container completely many times and then leaving it empty after 5 min. Cationic and anionic layers are added alternatively for 3 layers each with thorough rinse in between; the final coating is anionic. This PEM coating prevents adhesion of the colloidal gel to the container wall.

Syneresis Experiment

For a typical procedure of the syneresis experiment, a PEM coated and sealed spherical container with polystyrene (solid) particles dispersion at $\phi_0 = 0.01$ is submerged into the pre-heated water bath at 45°C . An image sequence is recorded with a ThorLab CMOS camera, as shown in Fig. 3.7. Syneresis of the three different particle gels at different volume fraction is captured with the same set-up, but with PEM coated cylindrical containers rather than spherical. For dispersions with $\Delta V/V_0 > 0.5$ in Fig. 3.4, volume of the colloidal gels after syneresis is calculated by extracting the projected area occupied by the gel from the images. For dispersions with $\Delta V/V_0 < 0.5$ in Fig. 3.4 and dispersions in the cycle experiments, expelled fluid is removed after each syneresis while the colloidal gel is still intact at temperature. Volume of the colloidal gels after each syneresis is calculated by weight deduction.

Figure 3.7: Set-up for syneresis movie recording; inset: illustration of the set-up from the side view.

Interdroplet Force Balance

Here we perform a force balance calculation between the interparticle attraction, $U \gg 50 k_B T$, developed at high temperature due to the thermoreversible surfactant, and the Laplace pressure of such small droplets. The force balance calculation between Laplace pressure and interparticle attraction, is described in work [12]. The force balance is,

$$\Delta F = 2\gamma(1 - \cos(\theta)) \quad (3.1)$$

where an inter-droplet “patch contact angle”, θ , interfacial tension, γ , and the force equal to the energy per unit patch area ($U(k_B T)/A$). We have independently measured $\gamma = 8.2 \text{ mN/m}$ between the continuous phase and polybutylacrylate solution using a pendent drop tensiometer. From this force balance, Eq. 3.1, using γ , and the measured interparticle force at 45°C [11], we calculate $\theta \sim 15^\circ$. In a seminal work in 1980 by H.M. Princen [18], the contact angle, θ , is related to the theoretical maximal packing fraction of deformable droplet; $\theta \sim 15^\circ$ res-

ulting in $\phi=0.82$, which corresponds extremely well to our observed maximal packing fraction as shown in Fig. 3.3.

Also stated in Princen's work "Whenever the contact angle is large, it is difficult to realize the high volume fraction predicted theoretically, because of the formation of a rather rigid floc network, trapping pockets of continuous phase that are not readily expressed, even by centrifugation." In these experimental conditions, the droplet system is able to explore such high-volume fractions due to the thermal cycling, which removes interparticle attraction, reducing the rigidity of the network, and returning to a low patch contact angle.

Rheology Measurement

Rheology measurements are performed on a stress-controlled rheometer (Anton Paar MCR 501) in a plate-plate geometry with a radius of 25 mm. Glass slides (25 × 25 mm) are coated with PEM ending with the polycation rendering the walls adhesive and then are stuck to both the top and bottom plates with double sided tape, to eliminate syneresis. A liquid particle dispersion is added and the temperature is risen from 25°C to 45°C in 10 minutes and held at 45°C for 3 hours during oscillatory shear measurements at a strain of 0.05% at a frequency of 1 Hz; the final value of G' is used in Fig. 3.5 (a). In all cases, a solvent trap is used to prevent solvent evaporation. Colloidal gels are formed *in situ* without loading history.

Micro-chamber for Quasi-2D Gel

The micro-chamber template is designed with AutoCAD. We use this design to create a photo-lithographic mask and fabricate a micro-chamber out of polydimethylsiloxane (PDMS) using standard soft lithography techniques [30]. The micro-chamber is plasma-bonded to a glass slide. Walls of the micro-chamber are PEM coated ending with the polyanion rendering the walls non-adhesive. Schematic illustration of the micro-chamber is shown in Fig. 3.8. We use an open-source PIV algorithm (pivLab) to analyse spatially and temporally resolved flow fields from time-lapse sequences recorded with light microscopy. The PDMS micro-chamber is heated at 45°C (OKO bold line) while imaging. The image sequences are recorded at 1 Hz.

Figure 3.8: Schematic illustration of the micro-chamber from both side and top view.

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CHAPTER 4

Gravity-driven Syneresis in Model Low-fat Mayonnaise

Low-fat food products often contain natural, edible polymers to retain the desired mouth feel and elasticity of their full-fat counterparts. This type of product, however, can suffer from syneresis: the compaction of a material accompanied by fluid expulsion. Gaining insight into the physical principles governing syneresis in such soft hybrid dispersions remains a challenge from a theoretical perspective, as experimental data are needed to establish a basis. In this chapter, we record non-accelerated syneresis in a model system for low-fat mayonnaise: a colloid polymer mixture, consisting of oil in water emulsion with starch in the aqueous phase. We find the flow rate of expelled fluid to be proportional to the difference in hydrostatic pressure over the system. The osmotic pressure of the added starch, while being higher than the hydrostatic pressure, does not prevent syneresis because the soluble starch is lost to the expelled fluid. From these findings, we conclude that forced syneresis in these systems can be described as gravity-driven porous flow through the densely packed emulsion, explainable with a model based on Darcy's law.

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4.1 Introduction

The acute awareness of the relationship between dietary fat and hypertension, the development of cardiovascular diseases, and obesity has stimulated the need among consumers for food products with reduced fat content [1, 2, 3]. To retain the desired mouth feel and elasticity of their full-fat counterparts, low-fat food products often contain natural, edible polymers [4]. Upon addition of these polymers, however, this type of products can suffer from syneresis: the compaction of a material accompanied by fluid expulsion, usually characterized by the appearance of the continuous phase at the bottom of a scoop, while the scoop retains its initial shape and does not flow on the macroscopic scale. Yet, on the microscopic scale, the material must undergo flow leading to progressive fluid accumulation at the bottom of the scoop, which is considered undesirable. Understanding the physics that govern this phenomenon is crucial to predict and control the properties of such soft hybrid dispersions for product stability against scoop syneresis.

Mayonnaise is an oil in water emulsion comprised of dispersed sunflower oil droplets suspended in a continuous phase of water, and stabilized by egg yolk proteins and phospholipids. The rheology of an emulsion depends strongly on the volume fraction of the dispersed phase: at approximately 80 vol% of the dispersed phase, typical of mayonnaise, oil droplets pack together, causing deformation of their interfaces. This repulsive force between the jammed droplets gives mayonnaise its elastic behavior. Syneresis does not occur in such full-fat mayonnaise, as an expulsion of fluid requires an applied pressure in excess of the droplet Laplace pressure to further deform the close-packed individual droplets; the scoop-induced hydrostatic pressure difference is a few orders of magnitude lower than the droplet Laplace pressure. When decreasing the volume fraction of the dispersed phase below a critical value, however, the elastic modulus decreases significantly [5, 6]. To recover the elasticity at low volume fraction, water-soluble (bio)polymers are added. Being an abundant, affordable and natural edible polysaccharide, starch is widely used to control the stability and texture of many food products [7]. Starch is a complex composite system, composed of amylose and amylopectin, occurring naturally as insoluble, semi-crystalline granules [8]. After heating in water, the starch suspension converts into a turbid viscoelastic paste, in which starch exists in various forms: water-soluble individual polymers,

water-swollen starch microgels, and water-insoluble granules [9]. At sufficiently high starch concentrations a network forms, consisting of an amylose matrix with deformable swollen granule fillers [10]. In addition to the network constructed by starch, soluble starch polymers induce depletion attraction between oil droplets. When droplets are at high enough volume fraction, they may form a space spanning, dynamically arrested network, which can form a colloidal gel [11, 12, 13]. Both of these networks impart elasticity to the low-fat mayonnaise. Yet, if this elasticity is of insufficient magnitude or breaks down when stressed, the product may experience syneresis. Syneresis is a dynamic process that depends on the interaction forces between the structural elements of the system and external driving forces, such as hydrostatic pressure difference [14].

While numerous studies have shown that syneresis of casein gels in cheese is due to rearrangements of the network of casein particles in response to internal stresses, forced syneresis in colloid polymer mixtures like low-fat mayonnaise under external stresses remains largely unexplored [15, 16, 17]. A common approach in studying syneresis is through accelerated measurements, such as centrifugation, which can be powerful for certain types of instabilities of food emulsions [18, 19]. However, the magnitudes of the forces involved in the force balance governing syneresis are not necessarily accelerated proportionally, which may lead to different conclusions in accelerated compared to non-accelerated tests.

In this chapter, we follow the syneresis of model low-fat mayonnaise systematically under hydrostatic pressure difference in a non-accelerated fashion. We explore the effect of added starch on the osmotic pressure and the elasticity of the material and investigate the composition of the expelled fluid during syneresis. Our results indicate that syneresis can be described as a gravity-driven flow of fluid through a porous medium formed by the hybrid colloid polymer network.

4.2 Results & Discussion

Driving Force for Scoop Syneresis

Our forced syneresis experiment is illustrated schematically in Fig. 4.1. Model low-fat mayonnaise is poured into a 3D printed container immediately after pre-

Figure 4.1: (a-c) Schematic depiction of the scoop syneresis experiment. (a) Black, yellow, green and grey represent, the outer reservoir, the model low-fat mayonnaise, the 3D printed inner tube and the filter paper, respectively. (b) After one week, model low-fat mayonnaise is aspirated from the inner tube. (c) Over time, fluid is expelled into the inner tube through the filter paper, as depicted in blue. (d) Weight of the expelled fluid in the inner tube as a function of storage time for different heights of the inner tube, h . Error bars represent standard deviation ($N=2$), which are smaller than the marker size.

paration; this container has two chambers, a smaller inner tube of a total height h , and a larger outer reservoir (Fig. 4.1 (a)). The sample is then left to set in the container for one week which allows the microstructure to fully form. After this equilibration period, the material in the inner tube is removed by aspiration to establish a hydrostatic pressure difference, Δp (Fig. 4.1 (b)). This height difference mimics a consumer scoop taken from mayonnaise. A gradual accumulation of fluid in the inner tube is observed (Fig. 4.1 (c)), which we monitor by carefully measuring the weight of the expelled fluid as a function of time (Fig. 4.1 (d)). The fluid expulsion continues for a long time and does not appear to be reaching an equilibrium value, even after 105 days. After a certain period, which is dependent on h , the weight of the expelled fluid appears to be increasing at a near

Figure 4.2: (a) Flow rate of the expelled fluid (solid circles), calculated from the weight of the expelled fluid as a function of the height of the inner tube. The red line represents a linear fit to the data, excluding $h > 4$ cm. Predicted flow rate of the expelled fluid (open squares) based on the two-region model later discussed in subsection Two-region Model for Forced Syneresis. (b) Weight of the expelled fluid, w_{ex} , normalized by the maximum weight of expelled fluid, w_m , as a function of storage time for different heights of the inner tube. Error bars represent standard deviation ($N=2$). The normalized weight for the first 16 days is shown in the inset.

constant rate. This rate is approximately proportional to the height difference h , as shown in Fig. 4.2 (a). Only for $h > 3.5$ cm, we find the rate of syneresis to decrease, which might be due to the bottom of the inner tube being spatially close to the bottom of the outer reservoir (the total height of the container is 4.75 cm). The initial linear increase with h is in line with the hypothesis that syneresis in these experiments is driven by the difference in hydrostatic pressure: considering the process as the gravity-driven flow of fluid through a porous medium formed by the droplets and starch network, we expect from Darcy's law a volumetric flux $Q_s = C\Delta p$, with the proportionality constant C dependent on the permeability of the sample, the geometry of the flow field, and the viscosity of the fluid. Since $\Delta p \sim h$, these results indicate that the proportionality constant C is independent of the height.

To further test this, we normalize the expelled weight for each tube height by the theoretical maximum of expelled fluid for that height w_m . The latter corresponds to the state where the hydrostatic pressure difference has vanished com-

Figure 4.3: (a) Weight change of starch suspensions of 2, 4 and 6 wt% after 8 days of storage normalized by initial weight as a function of the osmotic pressure of dialysis solution. Extrapolated points represent the osmotic pressure, as shown in open symbols. Zero weight change is depicted as a grey dashed line. The increase in starch weight percentage is indicated by the darkening shade of green. (b) Extrapolated osmotic pressure of starch suspension after 24h dialysis as a function of weight percentage on storage day 1 (circle), day 8 (square) and day 15 (diamond). The hydrostatic pressure difference, Δp , for $h = 4.5$ cm is depicted as red dashed line.

pletely and is approximately proportional to the tube height h . The normalized syneresis curves indeed collapse for a range of tube heights (2 to 4 cm), reflecting that they share the same normalized flow rate $Q_s/\Delta p$, as illustrated in Fig. 4.2 (b). For the two smallest heights, we see a different behaviour: during the first couple of days, almost no fluid is expelled and syneresis only starts after this delay time. This suggests that there is an energy barrier for syneresis to initiate, which is difficult to overcome if the driving force is small. Nevertheless, after this initial phase, all samples show the same normalized flow rate, which slowly changes over a period of a few months. We note that the driving force Δp changes by at most 25% during the first 100 days, since the amount of expelled fluid after 100 days is about 25% of the maximum (Fig. 4.2 (b)).

Osmotic Resistance against Scoop Syneresis

The picture of forced syneresis as hydrostatically driven fluid flow through a porous medium ignores the presence of an osmotic pressure difference between

the expelled fluid and the model low-fat mayonnaise. Fluid will be expelled only if the hydrostatic pressure difference is larger than the osmotic pressure difference. Conventionally, osmotic pressure is measured by dialysis when at equilibrium, where there is no mass transfer between inside and outside of a dialysis membrane. However, starch is known to retrograde during storage [21], which may complicate the determination of the osmotic pressure of starch suspensions. We establish a method for determining osmotic pressure under non-equilibrium conditions by dialysis for slurry-like materials. Method validation is explained in the Appendix with Fig. 4.6 (a). Starch suspensions of 2, 4 and 6 wt% after 8 days of storage are dialyzed against PEG solutions of known osmotic pressure: 1 kPa, 3 kPa and 5 kPa. These pressures are used to limit the volume change of the cassette, which may cause an error in determining the weight change. The weight change of the cassette after 24h of dialysis, normalized by the initial weight as a function of the osmotic pressure of the dialysis solution, is shown in Fig. 4.3 (a). The duration of dialysis is chosen to be 24h, a compromise between the measurable quantity of weight change and the retrogradation rate of starch. The osmotic pressure of the solution inside the cassette can be found by extrapolation (red dash lines) to the point where there is no weight change during the dialysis, indicated by the grey dashed line in Fig. 4.3 (a). At this point, the osmotic pressures inside and outside the cassette are equal. The extrapolated osmotic pressure of 8 days old starch suspensions with 2, 4 and 6 wt% are depicted by the open symbols in Fig. 4.3 (a).

Utilizing this extrapolation method, we find that starch suspensions after 24h of dialysis show an increasing osmotic pressure with increasing starch weight percentage, depicted in Fig. 4.3 (b). The osmotic pressure of starch suspensions decreases as the storage time increases as shown in Fig. 4.3 (b); this is likely to be a consequence of starch retrogradation during storage [21]. After 8 days, the osmotic pressure of a 4 wt% starch suspension is approximately 1.1 kPa, which is larger than the largest Δp set by the height difference in the scoop syneresis experiments, i.e. 0.45 kPa for the 4.5 cm tube as depicted by the red dashed line in Fig. 4.3 (b). This would imply that there should be no fluid expelled under the hydrostatic pressure difference in the scoop syneresis experiment.

However, in our syneresis experiments, we do observe the expulsion of fluid,

Figure 4.4: (a) Storage moduli G' (circle) and loss moduli G'' (diamond) of 4 wt% native rice starch suspension (open symbols) and model low-fat mayonnaise (solid symbols) as a function of shear strain amplitude. (b) Shear rate of 4 wt% native rice starch suspension (open symbols), model low-fat mayonnaise (black solid symbols) and aqueous phase (grey solid symbols) as a function of shear stress.

which suggests that the actual difference in osmotic pressure between the expelled fluid and the model low-fat mayonnaise is much smaller. This can be explained if the filter paper is permeable for the soluble component of the starch suspension. Since the osmotic pressure is determined by the number density of molecules, only the soluble fraction of starch contributes significantly to the osmotic pressure of the suspension, while the insoluble granules hardly affect the osmotic pressure. To validate this, we perform a series of tests to investigate the composition of the expelled fluid, delineated in the Appendix with Fig. 4.6. The purple color during an iodine test indeed confirms the presence of starch in the expelled fluid (Fig. 4.6 (b)), while thermogravimetric analysis (Fig. 4.6 (c)) and gel permeation chromatography (Fig. 4.6 (d)) indicate that the majority of the soluble starch leaves together with the fluid during the scoop syneresis experiment. We, therefore, assume that the osmotic pressure of the expelled fluid does not differ significantly from that of the model low-fat mayonnaise and that the osmotic pressure does not influence the syneresis process.

Shear Elasticity and Yield Stress

Another factor that could resist syneresis is the elasticity of the starch network [22]. As fluid is expelled, the volume of the hybrid emulsion-starch network decreases, and the resulting compression could lead to an elastic restoring force. To measure the elasticity, we perform rheology experiments on 4 wt% starch suspensions and on our model low-fat mayonnaise, consisting of dispersed oil droplets with 4 wt% starch. For both materials, storage moduli and loss moduli as a function of shear strain are shown in Fig. 4.4 (a); the storage moduli remain constant, eventually decreasing when the material yields with a corresponding increase in the loss moduli. These features fit the behavior of a soft glassy material [23]. Model low-fat mayonnaise has an overall higher storage modulus compared to a 4 wt% starch suspension, implying that an additional network contributes to the elasticity of the model low-fat mayonnaise. Additionally, the yield strain, where the storage modulus starts to decrease, is smaller for the model low-fat mayonnaise than for the 4 wt% starch suspension (Fig. 4.4 (a)). Indeed, colloidal gels have been shown to be fragile in shear strain [15, 24]. These observations thus suggest the presence of a space spanning colloidal network, induced by a depletion attraction between the fat droplets caused by the soluble fraction of starch in the model low-fat mayonnaise [25, 26, 27]. Alternatively, the higher storage modulus in model low-fat mayonnaise compared to 4 wt% starch could be a rigid filler effect for composite suspensions and gels due to the small size and resultant high Laplace pressure of the oil droplets [28]. In this case, the relation between the shear moduli and the volume fraction of oil would be described by the empirical Krieger-Dougherty relation [29]. However, experimental G^* results could not be fitted with this relation (Fig. 4.7 in the Appendix), indicating that the increase in modulus is more likely due to network formation of the oil droplets.

The presence of a colloidal droplet network could prevent droplets from flowing together with the fluid during syneresis. To verify this, we test whether the model low-fat mayonnaise has a yield stress that resists the flow of low-fat mayonnaise as a whole. A stress sweep is performed to model low-fat mayonnaise, aqueous phase and 4 wt% starch suspension; the shear rate of each material as a function of shear stress is shown in Fig. 4.4 (b). The yield stress of the mater-

ial can be estimated as the stress at which $\dot{\gamma} \simeq 10^{-3} \text{ s}^{-1}$ can first be measured in Fig. 4.4 (b). The apparent yield stress of model low-fat mayonnaise found in this way is higher than that of 4 wt% starch suspension. Notably, both these materials have a relatively low yield stress compared to full-fat mayonnaise and low-fat mayonnaise with other added polymers [30]. The smallest Δp in the scoop syneresis experiment, from the 1 cm inner tube, is 100 Pa, which is much higher than the measured yield stress of 0.3 Pa for the model low-fat mayonnaise, implying that the model low-fat mayonnaise should flow even under the smallest hydrostatic pressure difference.

Two-region Model for Forced Syneresis

The scoop syneresis experiment showed that the rate at which fluid is expelled initially decreased and then reached a constant value (Fig. 4.1 (d)), with a final syneresis rate that is proportional to the height difference h (Fig. 4.2 (a)). To explain these findings, we consider a simple model for flow through a porous medium. We assume that syneresis is driven by the hydrostatic pressure difference $\Delta p = \rho g(h - x)$ where x is the height of the expelled liquid column in the inner tube. Since the hydrostatic pressure difference in all our experiments is much larger than the yield stress of the model low-fat mayonnaise, the emulsion will flow as a whole towards the filter paper. While the continuous phase is expelled, the oil droplets accumulate near the filter paper and form a compacted zone of densely packed droplets. The Laplace pressure of the droplets, $\gamma/2R \sim 10^4 \text{ Pa}$ is much larger than the hydrostatic pressure difference so that the droplets will not deform significantly. We, therefore, assume that the volume fraction of droplets in the compacted layer is around random close packing, $\phi_{rcp} \approx 0.64$. As time progresses, the volume of this compacted zone grows. Further syneresis proceeds by the flow of the continuous phase through this compacted porous bed formed by the compacted droplets. We confirmed that the resistance of the filter paper is negligibly small and that no clogging of the filter paper occurs, explained in the Appendix with Fig. 4.8, so that the syneresis rate is determined completely by the flow rate of liquid through the porous bed formed by the densely packed droplets.

The geometry of the experimental set-up leads to a confinement of the flow

Figure 4.5: (a) As fluid flows out of the model low-fat mayonnaise, two regions of flow can be distinguished: a flow region of length d which is on average horizontal, and a vertical region whose length equals the height of the mayonnaise column. (b) The two-region model abstracts the 3D fluid flow of the experimental geometry as a 1D flow through two separate regions with unequal cross-section. The horizontal region of length d ends at the filter paper of surface area A_{in} , thereby setting its cross-sectional area. The vertical region has a cross-sectional area $A_j - A_{in}$, with A_j the total surface area of the container, coinciding with the area of the mayonnaise column as seen from the top. As the fluid is expelled, a layer of compacted mayonnaise with length $y(t)$ arises in the model low-fat mayonnaise. (c) Weight of the expelled fluid, w_{ex} , normalized by the maximum weight of expelled fluid, w_m , as a function of storage time for $h = 1$ cm (yellow) and 3 cm (red). Dashed lines mark w^*/w_m . Shading area represents stage 1. Solid linear lines are guides to the data in stage 2. Error bars represent standard deviation ($N=2$).

towards the filter paper. To account for this geometrical effect in a simplified manner, we develop a 1D-model, in which we divide the flow into two regions: (1) a region right below the filter paper of length d and cross-section A_{in} where the flow is mostly horizontal, and (2) a region of length h and cross-section $A_j - A_{in}$ that represents the top part of the container, where the flow is mostly vertical (Fig. 4.5 (a,b)). Mass balance implies that the velocities in the different zones are related as

$$A_{in}\dot{x} = A_{in}q_h = (A_j - A_{in})q_v \quad (4.1)$$

where $\dot{x}$ is the rate of change of the expelled liquid height and q_h and q_v are the fluxes in the horizontal and vertical regions, respectively, expressed in m/s. Note that $(A_j - A_{in}) \approx 10A_{in}$ in our experiments, so that $q_h \gg q_v$. The thickness of the compacted region is indicated as $y(t)$; this thickness grows as syneresis proceeds. Depending on the magnitude of $y(t)$, we consider two different stages

of the process.

Stage 1: $y(t) < d$

If $y < d$, the compacted region is present only in the horizontal region. The volume of the expelled fluid is equal to the volume with which the sample has shrunk due to compaction, so that $x(t) = \Delta\phi y(t)$, with $\Delta\phi = \phi_{rcp} - \phi_0 \approx 0.12$ and $\phi_0 = 0.52$ the initial volume fraction of oil droplets. Assuming that the flow through the compacted layer can be described by Darcy's law, we get

$$q_h = \frac{k\rho g(h-x)}{\eta y} \quad (4.2)$$

with k the permeability of the compacted layer, η the viscosity of the expelled layer and $\rho g(h-x)/y$ the pressure drop over the compacted region. With $q_h = \dot{x}$ and $y = x/\Delta\phi$ this can be written as

$$\dot{x} = \frac{k\Delta\phi\rho g(h-x)}{\eta x} \quad (4.3)$$

In the scoop syneresis experiment, the height of the expelled fluid column remains much smaller than h , so that $h-x \approx h$. With this, the solution of equation 4.3 is

$$x(t) = \sqrt{\frac{2k\Delta\phi\rho g h t}{\eta}} \quad (4.4)$$

In this regime, the rate of syneresis $\dot{x}$ is very large initially and then slows down. At time $t = t^*$, the compacted layer reaches the size of the horizontal region, $y(t^*) = d$. The corresponding height of the liquid column is then $x^* = d\Delta\phi$; with d on the order of $R_{in} = 1$ cm, this gives a value for x^* on the order of 1 mm.

Stage 2: $y(t) > d$

Since $x^* \ll h$, the compacted layer will grow further into the vertical region. The flow now corresponds to two porous layers in series, and the pressure drop is distributed between these two layers. For the horizontal region of size d , Darcy's law gives

$$q_h = \frac{k\rho g(h-x)\chi}{\eta d} \quad (4.5)$$

where χ is the fraction of the pressure drop over the horizontal region. For the vertical region this becomes

$$q_v = \frac{k\rho g(h-x)(1-\chi)}{\eta(y-d)} \quad (4.6)$$

where $y-d$ is how far the compacted region has grown into the vertical region. From Eq. 4.1 we see that $q_v \ll q_h$, since $A_j - A_{in} \gg A_{in}$. It follows from this that most of the pressure drop occurs over the horizontal region, $\chi \approx 1$. With $\dot{x} = q_h$, and again taking $x \ll h$, we obtain

$$\dot{x} = \frac{k\rho gh}{\eta d} \quad (4.7)$$

Hence, in this second stage, the syneresis rate is constant and proportional to the height h . Obviously, the syneresis rate will decrease further when x becomes comparable to h , leading to a decrease in the driving force.

Comparison to experiments

This two-region model gives an explanation for the experimental findings. As long as the compacted region remains in the horizontal region, the syneresis rate slows down due to the growth of the compacted region (Eq. 4.4). However, when the compacted region enters the vertical region, the syneresis rate stabilizes, because the flow rate in the vertical region is much lower than in the horizontal region. The cross-over between the two stages occurs when $x = x^* = \Delta\phi d \approx 1$ mm, which corresponds to a weight $w^* = \rho x^* A_{in} \approx 0.3$ g. This is reasonably close to the expelled fluid weight at which the experimental syneresis rate stabilizes. w^*/w_m is calculated for $h = 1$ cm and 3 cm, shown in Fig. 4.5 (c) as dashed lines. Compared with the w_{ex}/w_m data from the scoop syneresis experiment, it fits reasonably well to where the flow rate starts to be constant, indicating that around w^* the transition from stage 1 to stage 2 happened. In the second stage, the rate is proportional to h (Eq. 4.7). Experimentally, we find $\dot{x}/h = (dw_{ex}/dt)/\rho A_{in} h \approx 2 \cdot 10^{-8} \text{ s}^{-1}$. The porosity of the compacted region can be estimated from the Kozeny-Carman equation for packed spheres:

$$k = \frac{\langle R^2 \rangle (1 - \phi_{rcp})^3}{45 \phi_{rcp}^2} \quad (4.8)$$

Using $\phi_{rcp} = 0.64$ and $\langle R \rangle = 3 \mu\text{m}$ (Fig. 4.9 in the Appendix), we obtain $k = 2 \cdot 10^{-14} \text{ m}^2$. Since the expelled fluid comes from the aqueous phase, we estimate the viscosity of the expelled fluid as the low-shear viscosity of the aqueous/continuous phase, $\eta \approx 1 \text{ Pa}\cdot\text{s}$ (Fig. 4.4 (b)). This estimate should be considered as an upper bound, because the aqueous phase contains insoluble components, e.g. water-insoluble starch granules, which are not present in the expelled fluid. By applying the estimated k , we can calculate the constant flow rate in stage 2 for all the heights of the inner tubes based on Eq. 4.7. The calculated flow rates are shown in Fig. 4.2 (a) as open squares and are in good agreement with the experimental data, solid circles in Fig. 4.2 (a). Furthermore, using this estimate of η , we find $d \approx 1 \text{ cm}$, which corresponds to the radius of the inner cylinder, A_{in} . The two-region model thus gives a very good description of the experimental results utilizing the experimental dimensions and known values.

4.3 Conclusion

We have presented data and analysis which show that syneresis in colloid polymer mixtures like low-fat mayonnaise can be described as a gravity-driven flow of the continuous phase through a densely packed region of particles. A simple 1D-model based on Darcy's law, which accounts for the geometry of the flow field, gives a very good description of the final syneresis rate. For small applied pressures, however, we find a delay period before syneresis starts, indicating that there is an additional energy barrier. This barrier could be related to a delayed collapse of the colloidal network [31, 32]. It will be interesting to study how these findings are modified for systems which have a yield stress that is on the same order of magnitude as the pressure that drives syneresis. These insights will help in the design of complex soft materials and products with predictable stability.

4.4 Materials & Methods

Scoop Syneresis

Model low-fat mayonnaise is formulated with 52 vol% sunflower oil and 48 vol% aqueous phase. The aqueous phase contains 4 wt% native rice starch, 7 wt% egg

yolk, 5 wt% vinegar and 2.8 wt% NaCl. Native rice starch (4 wt%) (Sigma Aldrich) is dispersed in Milli-Q water and heated at 90 °C for 5 min while gently stirring. The container is partially sealed with parafilm to reduce evaporation during heating. Milli-Q water is added afterward to compensate for evaporation, thereby retaining a 4 wt% starch suspension. Next, the starch suspension is cooled and equilibrated to 50 °C. The starch suspension is subsequently mixed with the egg yolk, NaCl and vinegar. The model low-fat mayonnaise is produced by the slow addition of oil into the aqueous phase while mixing with a Silverson L5M-A Laboratory Mixer with Emulsor Screens at 5800 rpm. The model low-fat mayonnaise is prepared in two batches with each batch serving as one of the duplicates in the syneresis experiments.

To study scoop syneresis in model low-fat mayonnaise systematically, we vary the hydrostatic pressure difference between the mayonnaise surface and the bottom of the scoop. To achieve this, we use 3D printed containers which have two chambers, a smaller inner tube and a larger outer reservoir (Fig. 4.1 (a-c)). The inner tubes have a diameter of 2 cm with different total heights, h : 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 cm. The inner tubes are sealed at the bottom with filter paper with a pore size of 4-7 μm . We pour the model low-fat mayonnaise into the container both inside and outside the inner tube (Fig. 4.1 (a)). After a week, model low-fat mayonnaise is aspirated from the inner tube so as to make the scoop, inducing a height difference between the surface of the model low-fat mayonnaise in the outer reservoir and the bottom of the inner tube (Fig. 4.1 (b)). The period of one week was chosen, because the sample has reached a quasi-steady state after one week, based on preliminary rheological measurements. During storage, the container is covered with a screwed lid and sealed with parafilm to prevent evaporation. We measure the fluid accumulated in the inner tube as a function of time (Fig. 4.1 (c,d)). All syneresis experiments are performed at room temperature.

Osmotic Pressure Measurement

To validate the osmotic pressure measurements, we use solutions of polyethylene glycol (PEG, 20,000 g/mol). PEG is dissolved in Milli-Q water to obtain solutions of 0.55 wt%, 1.5 wt%, 1.85 wt% and 2.9 wt%. The solutions have osmotic

pressures of 1 kPa, 3 kPa, 5 kPa and 10 kPa correspondingly. The relationship between the PEG concentration and the resultant osmotic pressure has been calibrated previously [20]. PEG solution of 1 kPa is transferred into the dialysis cassettes (Slide-A-LyzerTM, 10K MWCO, 30 ml, Fisher Scientific B.V.) and immersed in PEG solutions with 3 kPa, 5 kPa and 10 kPa. The weight change of the cassettes is then measured as a function of time until equilibrium is reached.

Next, native rice starch suspensions with 2, 4 and 6 wt% are prepared as described in subsection Scoop Syneresis. The starch suspensions are transferred into the dialysis cassettes and immersed in different PEG solutions of 3 kPa, 5 kPa and 10 kPa osmotic pressure. The weight change of the cassettes with starch suspensions after 24h of dialysis is measured.

Rheology Measurement

Rheology measurements are performed on a stress-controlled rheometer (Anton Paar MCR 501) with a concentric stainless steel cylinder geometry which has inner and outer cylinder radii of 8.33 and 9.04 mm, respectively, and a volume of 4.5 ml. Two tests are carried out. An oscillatory strain sweep from 0.01% to 1000% at a frequency of 1 Hz and a stress sweep from 0.001 Pa to 100 Pa are applied. In all cases, a solvent trap is used to prevent solvent evaporation. All suspensions are rejuvenated after loading by shearing ($\dot{\gamma} = 1 \text{ s}^{-1}$) for 5 min and left to relax for 30 min before commencing the measurement.

Appendix

Osmotic Pressure Methods Validation

To validate determining osmotic pressure under non-equilibrium conditions by dialysis, measurements are first performed with PEG, a polymer of which osmotic pressure in solution is stable over time. We use a PEG of 20,000 g/mol, which is of the same order of magnitude as the molecular weight of soluble starch [8]. A 0.55 wt% PEG solution in the cassette is dialyzed against solutions of known osmotic pressure of 3 kPa, 5 kPa and 10 kPa. The weight change of the cassette normalized by initial weight as a function of the osmotic pressure of the dialysis solution is shown in Fig. 4.6 (a). These pressures are used to limit the

Figure 4.6: (a) Weight change of 0.55 wt% PEG (M_w 20,000 g/mol) solution normalized by initial weight as a function of osmotic pressure of dialysis solution. Extrapolated points represent the equilibrium pressure, as shown in open symbols. Inset: Evolution of weight change of PEG (M_w 20,000 g/mol) solution normalized by initial weight for dialysis osmotic pressure of 5 kPa (light blue) and 10 kPa (dark blue). (b) Iodine test of control (i) and expelled liquid (ii) from the scoop syneresis experiment, as shown in blue in (iii). (c) Weight percentage of expelled fluid (-) and soluble fraction of 4 wt% starch suspension (-) as a function of time. (d) Apparent molecular weight from gel permeation chromatography for expelled fluid (-) and soluble fraction of 4 wt% starch suspension (-).

volume change of the cassette, which may cause error in determining the weight change. The osmotic pressure of the solution inside the cassette can be found by linear extrapolation to the point where there is no weight change during the dialysis. At this point, the osmotic pressures inside and outside the cassette are equal.

As depicted by the open symbols in Fig. 4.6 (a), the extrapolated osmotic pressure of 0.55 wt% PEG solution inside the cassette is approximately 1 kPa, which is in agreement with the previous calibration [20]. Moreover, weight change of 0.55wt% PEG (M_w 20,000 g/mol) solution normalized by initial weight as a function of dialysis time for dialysis solution with osmotic pressure 5 kPa and 10 kPa is shown in Fig. 4.6 (a) inset. Approximately the same osmotic pressure of 0.55 wt% PEG solution is obtained from the weight change data of 24h and 48h dialysis, representing before and after dialysis equilibrium respectively, as shown in Fig. 4.6 (a). This allows us to determine the osmotic pressure of starch suspension by the weight change data before dialysis equilibrium is reached, which reduces the possible change in osmotic pressure caused by starch retrogradation. This establishes a method for osmotic pressure measurements of slurry-like material, which cannot be measured with a membrane osmometer.

Composition Analysis of Expelled Fluid

A. Starch Test

A potassium triiodide solution of 0.1 M is prepared; 500 μ l of the potassium triiodide solution is added into both 1 ml of the expelled fluid from the scoop syneresis experiment and Milli-Q water. The color change of the solutions is recorded and visually inspected to test for the presence of starch (Fig. 4.6 (b) (i, ii)). The purple color in Fig. 4.6 (b)(ii) suggests the presence of starch in the expelled fluid.

B. Thermogravimetric Analysis

Thermogravimetric analysis is conducted with a Simultaneous Thermal Analyzer (STA) 6000 and Pyris software (Perkin Elmer, United Kingdom). A 4 wt% native rice starch suspension is prepared as stated in subsection Scoop Syneresis. For both the soluble starch and the expelled fluid sample, 20 mg is added into the sample holder and placed inside the STA. Samples are first held at 30 °C for 1 min and nitrogen is switched on at a flow rate of 30 ml/min. Next, a temperature ramp from 30 °C to 90 °C is applied at a rate of 10 °C/min, and finally the temperature is held at 90 °C for 15 min for complete evaporation of water. The sample weight is monitored and the solid content of the sample is calculated as the final weight divided by the initial weight. Weight percentage of

Figure 4.7: Relative complex modulus of 4wt% starch model low-fat mayonnaise as a function of disperse phase volume fraction. The red line represents the fit to the data by Eq. 4.9 with $\phi_m = 0.64$.

the expelled fluid and the soluble fraction of 4 wt% starch suspension as a function of time is shown in Fig. 4.6 (c). To calculate starch content in the expelled fluid, weight of NaCl is subtracted from the TGA data.

C. Gel Permeation Chromatography

A 4 wt% native rice starch suspension is prepared by bringing 0.4 g of starch to a volume of 10 ml Milli-Q water. The suspension is heated at 90 °C for 5 min under gentle stirring. After the suspension is cooled and equilibrated to 50 °C, it is centrifuged for 20 min at 10,000 g, and the supernatant is filtered through a 0.45 μm filter to prevent clogging of the column. The sample of expelled fluid from the scoop syneresis experiment is centrifuged and filtered with the same procedure. The filtered expelled fluid and starch solution (25 μl) are injected into a PL aquagel-OH mixed 8 μm 250 $\times$ 4.6 mm, PL1549-5801 column. The mobile phase is H₂O containing 0.05 wt% NaN₃ with a flow rate of 0.4 ml/min. A calibration curve relating the molecular weight to the retention time is obtained by using PEG solutions of known molecular weight. Apparent molecular weight of starch in the expelled fluid and the soluble fraction of 4 wt% starch suspension is shown in Fig. 4.6 (d).

Figure 4.8: Panel A. Results (a) and schematic illustrations (b and c) of the mayonnaise layer experiment to test whether clogging of the filter paper is significant. (a) Weight of expelled fluid from the tube into the jar as a function of time t . The expelled fluid weight in syneresis experiment ($h = 2$ cm) from Fig. 4.1 (d) is given for comparison. (b) The inner tube, of height $h = 2$ cm, is filled with starch suspension. (c) The tube is filled with starch suspension with a small layer of model low-fat mayonnaise in between the starch suspension and the filter paper. **Panel B.** Results (a) and schematic illustrations (b, c and d) of the experiments to test whether aspiration of model low-fat mayonnaise causes clogging of the filter paper. (a) Weight of expelled fluid from the tube into the jar as a function of time. (b) In the control experiment, the inner tube is filled with starch suspension. (c) The inner tube is first filled with model low-fat mayonnaise and left for one week. Afterwards, the mayonnaise is aspirated and replaced by starch suspension. (d) Same as c but both the inner tube and the jar are filled with mayonnaise.

Krieger-Dougherty Relation

The higher storage modulus in model low-fat mayonnaise compared to 4 wt% starch (Fig. 4.4 (a)) could be a rigid filler effect for composite suspensions and gels due to the small size and resultant high Laplace pressure of the oil droplets [28]. In this scenario, the relative complex modulus of composite suspensions/gels with solid viscoelastic particles ($G_f^* \gg G_m^*$)

$$G_r^* = \frac{(G_r^* - G_f^*/G_m^*)^{2.5}}{(1 - G_f^*/G_m^*)} \cdot \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5 \cdot \phi_m} \quad (4.9)$$

where G_r^* is defined as $G_r^* = G_c^*/G_m^*$ (G_c^* , G_m^* are the complex shear moduli of the composite suspension/gel and the matrix, respectively), G_f^* is the complex modulus of the filler particles. Eq. 4.9 is analogous to the Krieger-Dougherty relation. Since the filler can be considered as a rigid particle, $G_f^* \rightarrow \infty$, and the first term of Eq. 4.9 is reduced to one [29]. As shown in Fig. 4.7, the fitted G_r^* could not describe our experimental data.

Filter Paper Clogging Test

To test whether oil droplets clog the filter paper in the scoop syneresis experiment, several additional experiments are conducted. The model low-fat mayonnaise and starch suspension used are prepared as in subsection Scoop Syneresis. The starch suspension is added into the inner tube which is inserted into the jar and the weight of the expelled fluid is monitored. All the inner tubes are of the same height, $h = 2$ cm.

As a reference experiment, the inner tube is filled with starch suspension while leaving the jar empty (Fig. 4.8 Panel A (b)), and the expulsion of fluid into the jar is measured. Next, we filled the inner tube with starch suspension, but with a small, yet macroscopic, layer of model low-fat mayonnaise in between the starch suspension and the filter paper (Fig. 4.8 Panel A (c)). We measure, as a function of time, the weight of expelled fluid in the jar (Fig. 4.8 (a)). If oil droplets indeed clog the filter paper, the expelled fluid is expected, at least initially, to be similar to the scoop syneresis experiment in Fig. 4.1 (d) where model low-fat mayonnaise column has the same height $h = 2$ cm as the starch sus-

pension column. However, we observed that the experiment with model low-fat mayonnaise layer exhibits similar fluid expulsion as the experiment without (Fig. 4.8 Panel A (a)). As both the reference and the model low-fat mayonnaise layer experiment have a fluid expulsion rate of approximately an order of magnitude larger than the Scoop Syneresis experiment, these results suggest that the filter paper is not clogged by oil droplets.

In the scoop syneresis experiment mentioned in subsection Scoop Syneresis, model low-fat mayonnaise is aspirated from the inner tubes as to mimic the formation of a scoop. In principle, this aspiration may cause clogging by sucking droplets from beneath the filter paper through the filter paper. To test this, we conducted the following experiments. In an empty jar, model low-fat mayonnaise is added into the inner tube and is aspirated after a week and then replaced by starch suspension (Fig. 4.8 Panel B (c)). The same experiment is performed in a jar filled with model low-fat mayonnaise (Fig. 4.8 Panel B (d)). The expulsion characteristics of two experiments above are compared to the control experiment in which the inner tube is filled with starch suspension to start with (Fig. 4.8 Panel B (b)). As the difference in the fluid expulsion rates between the three experiments is negligible (Fig. 4.8 Panel B (a)), aspiration does not appear to clog the filter paper.

Cryo Scanning Electron Microscopy

Model low-fat mayonnaise is prepared as described in subsection Scoop Syneresis and pipetted into small brass sample holders. The samples are frozen by plunging the sample holders into liquid nitrogen. Subsequently the samples are transferred to a cryo-preparation chamber (Leica) under vacuum where they are fractured at -90°C and kept for 3 min to remove ice from the surface. Still under vacuum the samples are coated with 12 nm of tungsten by sputter coating and transferred under vacuum using a VCT100 shuttle (Leica) to a field emission scanning electron microscope (Magellan 400 from FEI). Samples are analysed at 2 KV, 6 pA at -120°C . The electron microscopy image is illustrated in Fig. 4.9.

Figure 4.9: Scanning electron microscopy image of 4 wt% native rice starch model low-fat mayonnaise, 52 vol% dispersed phase.

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CHAPTER 5

Unravelling Spatially Heterogenous Dynamics in Colloidal Gels during Syneresis

Syneresis, the compaction of a material accompanied by fluid expulsion, is a typical mechanical instability which exists among colloidal gel based materials and that negatively affects the quality of relevant applications. In this chapter, we shed light onto the internal dynamics of model colloidal gels undergoing syneresis using Laser Speckle Imaging (LSI) with high spatial and temporal resolution. The resulting dynamical maps, d_2 , capture the distinct differences in spatial relaxation patterns between colloidal gels comprising of solid and liquid particles. This indicates different mechanisms of syneresis between the two systems and highlights the importance of the constituent particles and their mobile or restrictive interfaces in the mechanical relaxation of the colloidal gels during syneresis.

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5.1 Introduction

Colloidal gels are soft solids in which attractions between dispersed colloidal particles drive a thermodynamic instability that promotes aggregation, arriving at a space-spanning network structure, the unique mechanical and transport properties of which can be suitably tuned [1, 2]. Colloidal gels are widely encountered in applications such as drug delivery systems, food products, coatings, and more [3, 4]. While a colloidal gel forms, to minimize the interfacial energy cost in the network, particles tend to maximize contact with each other, leading to local compaction in the structure. The inhomogeneity of this compaction leads to randomly distributed regions of inhomogeneous deformations, each of which generates a displacement field around it due to the elasticity of the network. These inhomogeneities can then be considered as localized internal stress built within the network [5, 6]. When this internal stress is of sufficient amplitude or is facilitated by external stress, colloidal gels may suffer from a specific mechanical failure known as syneresis [7, 8], i.e. the contraction of the material accompanied by the expulsion of fluid. Syneresis is a typical mechanical instability encountered in food colloids, which is characterized by the appearance of fluid after a scoop in products like yoghurt and low-fat manufactured food. Unlike yielding of a solid network and fluidization of a gel induced by applied strains, the syneresing material itself does not necessarily undergo a solid to liquid transition, which indicates that the governing mechanisms are different than for strain induced yielding.

Syneresis has been studied most intensively on macroscopic samples such as cheese and yoghurt, a colloidal gel formed by casein micelles. To date, the investigations have been centered on bulk syneretic properties, i.e. dimensional changes, rate of fluid expulsion and structural rearrangement obtained indirectly by rheology [9]. Correlations have been found between the expulsion of fluid and parameters like pH and temperature [10, 7, 11]. Internal stresses and external stresses applied to the material robustly influence the magnitude of syneresis [12, 13]. Rearrangements of the network play a crucial role in determining the ease of fluid expulsion; $\tan\delta$ which represents the ratio of the dissipated energy due to relaxation of interparticle bonds and the energy elastically stored caused by a small distortion of the bonds is probed via rheology as an indica-

tion of structure changes [10, 14]. Such ensemble measurements, however, do not provide spatial information of the material undergoing syneresis. More specifically, it is not clear over what distance into the sample syneresis occurs and over what time scale. When syneresis occurs, while the material may retain its initial shape and does not appear to flow on the macroscopic scale, on the microscopic scale the material must undergo rearrangements leading to progressive fluid expulsion. Arriving at a deeper understanding of the relationship between microscopic dynamics and bulk syneresis in a colloidal gel is a crucial step in the endeavour towards understanding the mechanical response of colloidal materials.

Understanding how the fluid and particle dynamics at the microscale govern syneresis is challenging as it involves a wide range of time and length scales, which calls for methods in which the rich spatiotemporal heterogeneities can be directly and quantitatively visualised. Conventional optical microscopy often fails at this task due to the inherent turbidity of colloidal gels and related commercial products, which causes multiple scattering of light and insufficient light transmission. We therefore apply a different technique, Laser Speckle Imaging (LSI), which makes use of the turbidity to resolve the hidden dynamics within non-transparent materials and is the imaging counterpart of Diffusive Wave Spectroscopy in essence [15]. LSI has been widely applied in medical imaging since the 1980s to visualise, for instance, subcutaneous flow of blood [16, 17, 18, 19], but in the last a few years it has been also used to look at phenomena such as self-healing of polymers and delayed fracture in soft solids [20, 21]. The technique relies on the illumination of a material with an expanded beam of coherent light. The photons of the coherent light are scattered multiple times by the optically turbid material and then the back-scattered light is captured by a camera. As the illuminating light is coherent, interference of these scattered waves creates a pattern known as a speckle image. In an evolving sample, the shape of the speckle pattern changes, which creates contrast for dynamic analysis [22, 23]. LSI thus uses changes in photon path-length to gather information on nanoscale movement at very high temporal and spatial resolution. With LSI, dynamical processes at different length scales, such as Brownian motion, flow, and deformation can be distinguished and quantified.

Figure 5.1: (a) Schematic illustration of back-scatter LSI set-up. The syneresis sample is illuminated with a coherent plane light wave, which is multiply scattered by the turbid sample, giving rise to a raw speckle image captured by the camera; (b) Example images of a raw speckle image, a binary threshold mask and resultant image of multiplying the mask to the d_2 map. Each purple rectangle represents one image.

In this chapter, we use Laser Speckle Imaging (LSI) to create highly resolved dynamic maps of model colloidal gels and commercial yoghurt during syneresis. These measurements allow for identification of the microscopic dynamics that govern syneresis.

5.2 Results & Discussion

Syneresis d_2 Map

Dispersions consisting of polystyrene particles (PS) or polybutylacrylate particles (PBA) with an averaged radius, $\langle r \rangle = 275$ nm, at $\phi=0.01$ and 0.02 respectively in a density matched solution are prepared in non-adhesive capillaries. Both types of particles have $0.1\text{wt}\%$ of a thermoresponsive surfactant adsorbed onto their surface. Upon heating above 32°C , reversible and temperature-triggered adhesive forces are induced between the particles, with an attractive strength $\gg k_B T$ [24, 25], leading to the formation of a colloidal gel (Chapter 3). Immediately after formation, gels undergo compaction, expelling the continuous fluid as seen in the recorded movie.

We start an LSI measurement by heating a climate chamber which contains all of the optical elements and the sample. Data collection begins when the temperature in the climate chamber reaches 32°C. A coherent light illuminates the sample and back scattered light is detected by a camera, illustrated in Fig. 5.1 (a). Photon path length differences within the turbid sample generate an interference, or speckle pattern as shown in Fig. 5.1 (b). While the absolute intensities in the snapshots of the speckle pattern are irrelevant, information on the internal dynamics of the colloidal gel during syneresis in time and space is extracted from the raw speckle images by analyzing the temporal fluctuations in speckle intensity via the contrast function $d_2(t, x, y, \tau)$ [26, 27, 28]

$$d_2(t, x, y, \tau) = \frac{\langle [I(t, x, y) - I(t + \tau, x, y)]^2 \rangle}{\langle I(t, x, y) \rangle \langle I(t + \tau, x, y) \rangle} \quad (5.1)$$

where I is the speckle intensity at position (x, y) , t is the age of the sample which provides the temporal dimension and τ sets the time lag between which images are autocorrelated, and hence the relaxation time of the dynamics of focus; small values of τ correspond to fast, high-frequency dynamics, while large values of τ enable the study of low-frequency processes. Based on the d_2 , spatiotemporal maps of the dynamics can be created [29, 30]. High d_2 values indicate decorrelation of the signal and therefore enhanced dynamic activity. Due to the relative movement of the sample during syneresis, fluctuations occur in the void area in the field of view. The d_2 maps are therefore multiplied with a binary threshold mask, shown in Fig. 5.1 (b), to eliminate these fluctuations.

We monitor the syneresis process over time with LSI and compute d_2 values which encode the dynamics of the colloidal gel during syneresis. In Fig. 5.2, d_2 maps of PS and PBA colloidal gels ($\tau=0.125$ s) are illustrated as an example of the temporal development of dynamics during syneresis, where $t = 0$ min is defined as the moment when 32 °C is reached within the sample chamber. The edge of the colloidal gel is identical to the capillary wall at $t = 0$ min and moves as syneresis occurs. Compared with the PS gel, a more substantial syneresis is observed in the PBA gel, which manifests in higher d_2 values. During the first 8 minutes for the PS gel (Fig. 5.2 (a)), mobility increases within the entire sample while there is no sign yet of macroscopic syneresis. As syneresis proceeds, the colloidal gel detaches from the capillary wall and mobility in the bulk decreases,

Figure 5.2: Time-lapse d_2 maps of (a) PS and (b) PBA gel during syneresis, $\tau=0.125$ s, colormap inferno. Left end of d_2 maps represents the capillary wall. Activity band in the PBA gel is located with a white rectangle for $t = 26$ min.

while around the gel edge a relatively high mobility retains. For the PBA gel (Fig. 5.2 (b)), higher mobility emerges after 6 minutes, indicated by the higher d_2 value. The mobility near the gel edge remains high while the mobility in the bulk starts to decrease after 16 minutes, which is similar to the PS gel but the high activity region is of a wider range and occurs much earlier during syneresis. Meanwhile, a zone of increased activity develops behind the gel edge, which lingers until the end of syneresis (Fig. 5.2 (b), white rectangle). After 26 minutes, the rate of syneresis slows down and d_2 at the gel edge decreases as well. In general, the mobility in the bulk slows down faster than the mobility near the edge, suggesting that there is spatial dependence of the local dynamics during relaxation.

Figure 5.3: Profiles of normalized d_2 for the PS colloidal gel at different relaxation times as a function of distance to the moving edge for different sample age. $x(t) = 0$ mm represents the current edge.

Figure 5.4: Profiles of normalized d_2 for the PBA colloidal gel at different relaxation times as a function of distance to the moving edge for different sample age. $x(t) = 0$ mm represents the current edge.

Spatial Relaxation with Different Relaxation Times

For a more quantitative description of the spatial dependence of the local dynamics in the direction of syneresis as observed in Fig. 5.2, the normalized d_2

is computed and displayed as a function of distance to the moving gel edge, x , for different t in Fig. 5.3 and 5.4, for PS and PBA gels, respectively. As shown in Fig. 5.3, for the PS gel, the dynamic activity decreases gradually away from the edge in a similar manner for all τ , implying that different types of dynamic processes have similar spatial dependence. In contrast to the dynamics in the PS gel, the normalized spatial d_2 profile is much more diverse in the PBA gel (Fig. 5.4), showing a band of enhanced dynamics a few hundred microns behind the edge of the gel, which we call the activity band (Fig. 5.2 (b), white rectangle). The activity band already rises for small τ at 11 minutes and appears in all τ after 21 minutes. Also the spatial d_2 pattern shows a dependence on τ , which suggests that different dynamic processes occur in different locations.

To investigate the distinct spatial dependence of d_2 between the two types of colloidal gels, we take a closer look at the activity band in the PBA gel. Firstly, the position of the peak of the band and the moving edge with respect to the capillary wall is calculated; the macroscopic motion of the whole gel is substantial, as indicated by the distances from the moving gel edge to the capillary wall as a function of t in Fig. 5.5 (a) (dashed line). For all the calculated τ , the activity band grows further away with respect to the moving gel edge in the first 20 minutes and retains the same distance to the gel edge as the macroscopic movement of the gel stops, as indicated by the plateau for the later ages in Fig. 5.5 (a). As illustrated in Fig. 5.4, the shape of the activity band also changes over time. To study the evolution of the activity band for different τ , we calculate the full width at half maximum (FWHM) and the asymmetry ratio of the activity band distribution as a function of t , depicted in Fig. 5.5 (c,d). An example of determination of the FWHM and the ratio is shown in Fig. 5.5 (b) with $\text{FWHM} = x_2 - x_1$ and asymmetry ratio $= \sigma_2/\sigma_1$. A ratio below 1 indicates that the majority of the rise in mobility is on the left side of the band, nearest to the moving edge, not the gel side of the sample. We note that the ages before the complete development of the activity band for different τ are neglected, as seen in Fig. 5.4. The activity band develops earlier for the three smaller τ ; the width of the band increases with the macroscopic compaction of the gel. For the two larger τ , the activity band widens after the macroscopic compaction subsides with increasing t . An opposite trend in FWHM for the smallest and larger τ groups is observed, which

Figure 5.5: (a) Distance from the moving edge of the PBA (dashed line) and peak of the activity band (solid lines) to the glass capillary wall: the shrinkage of the sample over time is displayed together with the location of the highest value in the activity band, as a function of age, t . (b) Example for determination of FWHM and asymmetry ratio. (c) FWHM of the activity band over different τ as a function of t . (d) The asymmetry of the activity band distribution, represented by ratio $= \sigma_2/\sigma_1$, at different τ as a function of t .

might suggest different dynamics probed by these two relaxation time groups. In terms of the asymmetry ratio, for all τ at all times, the band is asymmetric, indicative of a difference in relaxation between the side to the gel edge and the side towards the bulk. For the majority of relaxation times, a wider width on the side of the gel edge in the band is detected. This may because the side to the gel edge

Figure 5.6: Profiles of normalized d_2 and the average light intensity as a function of distance from the moving edge. $x = 0$ mm represents the moving edge of the PS colloidal gel (a-c) at $t = 20, 35$ and 44 min and the PBA colloidal gel (d-f) at $t = 21, 26$ and 31 min.

is more elastic; when under stress, the stress is distributed over a larger length. We note that the noise in data of $\tau = 0.005$ s at later ages can be attributed to the flattening of the band, as shown in Fig. 5.4.

To examine the spatial variation in the density of the gel, we monitor the average light intensity. We assume that regions of high particle density scatter more strongly so that a higher average light intensity indicates a higher local particle volume fraction. Both the average light intensity and the profile of normalised d_2 ($\tau = 0.125$ s) are shown as a function of distance from the moving edge in Fig. 5.6. In all cases, we observe that the intensity decreases towards the edge of the gel. We believe, however, that this is not caused by a decrease in local density, but rather by an asymmetry in the photon paths: while photons can reach the detector from all directions in the bulk of the sample, locations near the moving edge only receive photons from the right, leading to a lower photon count in regions within a few l^* from the sample edge (at the edge, the intensity will be reduced by roughly a factor of two). We therefore disregard the region of lower intensity of approximately 300 microns near the edge. With these reservations, there is nevertheless a significant difference between the PS and PBA gels. While

in the PS gel, the apparent density is more or less homogeneous, for the PBA gel the density is reduced in the region where the dynamic activity is higher and slightly behind it. Hence, the dynamics appear to be faster in regions of lower density. The expulsion of liquid during syneresis inevitably increases the overall particle density. This process starts at the edge of the sample, as evidenced from the high activity during the first 20 minutes of syneresis. This increases the local density there; in the PBA gel this apparently leads to a very dense region at the front where the dynamics then slows down, probably because of the high elasticity [31]. Further compaction then needs to occur in the region behind this dense front, where the density is lower. In the PS gel we find a different scenario, with a more uniform compaction and the highest dynamics localized at the edge as syneresis proceeds to later age.

Governing Dynamics

To elucidate the nature of the observed dynamics, we extract the mean square displacement ($\langle \Delta r^2 \rangle$) of the particles from the LSI measurements based on contrast function, d_2 . A detailed explanation is delineated in the Materials & Methods section. The multi-speckle averaged $\langle \Delta r^2(\tau) \rangle$ for selected regions at different locations in both PS and PBA gels are shown in Fig. 5.7. For both the PS and PBA gel, we select a rectangular area in the bulk, parallel to, but as far away as possible from the gel moving edge, denoted as “bulk”. For the PBA gel, two more locations denoted as “band” and “valley” are defined, residing at the peak of the activity band and at the spatial average region between the moving edge and the peak of the activity band, respectively. All the rectangular areas have a dimension of 0.0625×3 mm.

For the PS sample (Fig. 5.7 (a)), $\langle \Delta r^2(\tau) \rangle$ show diffusive behaviour during the early ages, as evidenced from the slope close to 1. In later ages, the slope increases to around 2 for larger τ , indicative of ballistic motion, caused by the directional motion of the compacting gel. A transition from sub-diffusive to ballistic motion is observed in the PBA gels (Fig. 5.7(b)), although the initial diffusive regime is not observed here, probably because the elastic gel forms more rapidly for the PBA gel. Also, the transition to ballistic motion occurs sooner than for the PS gels, because syneresis happens more quickly for these samples. From these

Figure 5.7: Mean square displacement, $\langle \Delta r^2(\tau) \rangle$, of (a) PS gel in the bulk region during syneresis as a function of τ . Increasing shades of purple represents $t = 8, 13, 20, 35$ and 44 min; (b) of PBA gel in the bulk region, increasing shades of purple represents $t = 6, 11, 16, 21, 26$ and 31 min; (c) of PS gel at the edge (triangle) and bulk (circle) during syneresis as a function of τ at $t = 44$ min; (d) of PBA gel at the activity band (triangle), valley (pentagram) and bulk (circle) during syneresis as a function of τ . Closed and open symbols represent $t = 21$ and 26 min, respectively.

data, we conclude that syneresis is driven by directional particle movement at the microscopic scale.

Next, we compare $\langle \Delta r^2(\tau) \rangle$ in different locations in PS and PBA gel in the regime where syneresis occurs and directional motion is observed. For the PS

Figure 5.8: Schematic illustration of the sample chamber for yoghurt measurement; (a) before scoop; yoghurt (light yellow) is placed between two pieces of U-shaped PDMS (light grey) and (b) after scoop; white stripe in the middle of the chamber represents the deprivation of yoghurt. The red rectangle marks the field of view of LSI.

gel, at later ages during syneresis, $\langle \Delta r^2(\tau) \rangle$ decreases gradually with increasing distance to the gel moving edge, indicating that the particle velocity is highest near the edge and decreases towards the bulk of the sample (Fig. 5.7(c)). In the PBA gel, $\langle \Delta r^2(\tau) \rangle$ varies non-monotonically with the distance to the moving edge. $\langle \Delta r^2(\tau) \rangle$ at $t = 21$ and 26 minute in the PBA gel is illustrated in Fig. 5.7 (d) for valley, band and bulk regions. Here we focus on the directional motion. As expected from the higher volume fraction and lower d_2 , the valley region indeed has smaller $\langle \Delta r^2(\tau) \rangle$ than the band region. The smallest $\langle \Delta r^2(\tau) \rangle$ is found in the bulk region, furthest from the moving edge in the field of view. As gels compact towards the center, the further a region is away from the moving edge, the less directional motion there is during syneresis. The difference in $\langle \Delta r^2(\tau) \rangle$ between different regions grows larger as τ increases.

Yoghurt

With the information on spatial dynamics of model colloidal gels during syneresis at hand, we conduct a proof of concept LSI measurement to envisage dynamics in a commercial food product which undergoes syneresis. Yoghurt is a prototypical colloidal gel based food product, the quality of which is negatively affected by syneresis. Obtaining deeper insight into the spatially and temporally resolved dynamics during syneresis of such products benefits product design with improved mechanical stability. Yoghurt is situated in a sample chamber as illustrated in Fig. 5.8 and syneresis is triggered by “scooping”, which breaks the

Figure 5.9: Time-lapse d_2 maps of yoghurt during syneresis, from left to right, $t = 0, 6, 50$ and 226 h and from up to down, $\tau = 0.01, 0.1$ and 0.5 s, colormap fire. Right end of d_2 maps represents the interface generated by scooping.

force balance in the sample.

Spatially resolved d_2 maps of yoghurt during syneresis are depicted in Fig. 5.9 for different ages and relaxation times. The highest mobility is observed at the very early age of syneresis. We speculate that this is because the driving force is the highest at the time; the original force balance in the sample chamber is disturbed at the scoop, resulting in internal stresses which drive the previously arrested colloidal network to rearrange to a configuration at a lower energy level. As the material approaches the next energy minimum, the force balance is gradually restored, diminishing the driving force for syneresis. We note that there is a delay between the scoop and measured $t = 0$ h due to sample preparation. There is a clear mobility decrease from the moving sample edge into the bulk with a high activity band developed immediately next to the moving edge. The moving edge of this yoghurt sample is not as sharp as the model colloidal gels, indicative of interaction with the coated glass wall that is different from the model systems. We note that the uneven edge may be induced by evaporation. However, the recorded sample mass during the measurement suggests otherwise. Moreover, syneresis occurs over a much longer period with much lower velocity compared

Figure 5.10: Schematic illustration of a proposed scenario for the PBA and the PS gel during syneresis.

to the model colloidal gels. This may be attributed to the much more complex compositions of the commercial food products. From these preliminary results, LSI appears to reveal the internal dynamics for commercial food products that undergo syneresis, which is of particular importance for turbid samples; future studies on yoghurts with better defined ingredients would be valuable to investigate.

5.3 Conclusion

In this chapter, we have looked at the dynamics during syneresis in colloidal gels using a non-invasive technique, LSI. The spatially resolved d_2 maps allow

distinguishing relative differences in the dynamics between different locations in the sample. In the PS gel, different types of dynamic processes have similar spatial dependence and slow down gradually as a function of distance to the gel edge, while in the PBA gel, dynamic processes occur differently in different locations with the emergence of an activity band a few hundred microns behind the gel edge. Moreover, the PBA gel exhibits spatial heterogeneity in volume fraction during syneresis; a dense region between the gel edge and the activity band is followed by a lower density zone around the activity band location. The PS gel, by contrast, shows a more uniform density. This difference between the two types of gels may be attributed to the different particle nature, i.e. solid or liquid.

In Chapter 3, we found that gels comprising of liquid particles consist of strands that can bend easily and bear stress mostly by stretching particle bonds. By contrast, solid particle gels exhibit surface asperities and a lack of surface mobility, resulting in stress being born by bending of gel strands. We propose that this difference manifests in the spatial dependence of the dynamics during syneresis, as schematically illustrated in Fig. 5.10. Because the elastic resistance to compaction is lower for liquid (PBA) gels, these gels experience fast compaction locally near the gel edge, resulting in a dense region. After a while, compaction in this region slows down as a consequence of the elastic stresses, and further syneresis proceeds in the region behind the dense zone, visible as an activity band of enhanced dynamics. By contrast, solid (PS) gels resist stress to a higher extent, arriving at a compaction that happens more slowly. Possibly this allows for rearrangement of the material over longer length scales, so that the compaction occurs gradually throughout the sample. These differences may explain why syneresis is most readily observed in colloidal gels composed of liquid droplets, like yoghurt and cheese, and less for solid particles like paints and coatings. However, even in solid particle based colloidal gels, syneresis may still be appreciable as shown in these PS gels.

5.4 Materials & Methods

Sample Preparation

Poly(N-isopropylacrylamide)(pNIPAM) surfactant is synthesized according to a published method [25]. Polystyrene (PS) particles of 275 nm radius are synthesized using dispersion polymerisation of styrene (Sigma) at 80°C for 2 hours using AIBN (Sigma) as a radical initiator [32]. The dispersion is filtered and washed by centrifugation (3x) into 0.1 wt% pNIPAM surfactant and 100 mM NaCl solution to a final $\phi=0.2$. The recipe for the synthesis of polybutylacrylate (PBA) droplets by UV initiated emulsion polymerization is as follows: a disperse phase, comprising of butyl acrylate with 0.3wt% 2,2-Dimethoxy-2-phenylacetophenone as initiator, and the continuous phase, comprising of 3 mM NaCl and 1 wt% pNIPAM, are mixed with a ratio 1/4 (v/v%). The mixture is vortexed and then bath-sonicated at 10 °C for 25 min. After bubbling with N_2 for 10 min in a sealed vial, the mixture is exposed to UV light for 10 min while gently mixing at 10 °C. The mixture is left overnight for complete polymerization at room temperature. PBA has a low glass transition temperature (T_g) and thus exists as liquid at room temperature. The particles have an average radius, $\langle r \rangle = 275$ nm, as determined by dynamic light scattering. PBA droplets are filtrated and dialyzed against 0.1 wt% pNIPAM surfactant and 100 mM NaCl solution to a final $\phi=0.2$ approximately.

PEM coating is prepared according to the following procedure according to [33]: solutions of 1 wt% cationic polymer, polydiallyldimethylammonium chloride ($M_w = 4 \times 10^5 - 5 \times 10^5$ g/mol, Sigma), in 1M NaCl and 1wt% anionic polymer, sodium polystyrene sulfonate ($M_w \sim 2 \times 10^5$ g/mol, Sigma) in 1M NaCl are prepared. The solutions are filtered with 0.45 μ m hydrophilic filter. To begin the process, the glass container is cleaned using a plasma cleaner. This makes the glass anionic, negatively charged. Cationic polymer solution is first added to the container and then rinsed away with sufficient amount of deionized water by filling the container completely many times and then leaving it empty after 5 minutes. Cationic and anionic layers are added alternatively for 3 layers each with thorough rinsing in between. This PEM coating prevents adhesion of the colloidal gel to the wall.

Dispersions of PS particles, $\phi = 0.01$, and PBA droplets, $\phi = 0.02$, are

injected into PEM coated rectangular cross-section capillaries (Rectangle Boro Tubing, 0.90×9.0 mm). At both ends of the capillary a hydrophobic paste (Krytox GPL205) is applied to prevent adhesion to the epoxy gel (Devcon) for capillary closure. During the LSI measurement, samples are situated in a thermostatic chamber at 32°C .

Greek yoghurt (Dodoni, 10% fat) is chosen as the product has sufficient yield stress which prevents flow after scoop deformation and undergoes syneresis in its original container reasonably fast after disturbance. The product is placed inside a sample chamber as illustrated in Fig. 5.8. To induce syneresis, an imbalance of forces is created by sliding a piece of polydimethylsiloxane (PDMS) through the middle of the yoghurt to mimic a scoop. After the scoop is made, another glass plate is placed on top of the sample, the binder clips are attached and the ends are sealed with epoxy gel (Devcon) to prevent evaporation. Weight of the sample chamber is registered during the measurement. The field of view with LSI is marked with the red rectangle.

Laser Speckle Imaging and Analysis

The set-up of LSI is illustrated schematically in Fig. 5.1 (a). Coherent light ($\lambda = 532$ nm, Cobolt Samba, 1W) passes through a beam expander and illuminates the sample. The back-scattered light passes a linear polariser perpendicular to the polarisation of the incident laser beam, eliminating specular and low-order scattering paths. The back-scattered light is then captured by the camera. Technical details of the set-up are delineated in [28]. The samples are situated on a platform which is connected to a computer-controlled balance (Sartorius, model WZA224-NC), logging the sample mass with 0.1 mg resolution and 1 Hz frequency. A climate chamber is applied to the set-up, which controls the ambient temperature of the sample, as well as minimizes air convection and stray light.

The laser power, exposure time and frame rate are important for capturing the right information. To prevent blurring of the speckles and to capture fast changing speckles, the exposure time is set as short as possible where it could still cover the full dynamic range of the camera. This minimizes over- and under-exposure hence data loss. Two different cameras are used: (i) Dalsa Genie camera (Stemmer Imaging) for the PBA colloidal gel and yoghurt at 200 fps and 100 fps,

respectively. (ii) HiSpec 1 camera (Fastec Imaging) for the PS colloidal gel at 2000 fps. The field of view is 640×480 pixels (4×3 mm) with Dalsa Genie camera and 640×240 (4×1.5 mm) to diminish frame drops for the HiSpec 1 camera.

The contrast function, d_2 (Eq.5.1) is calculated to resolve dynamics during syneresis, which vary significantly in both time and space. Symmetric normalization, i.e. the numerators with the product of mean intensities at times t and $t + \tau$ is used instead of the square of the mean intensity, which diminishes drift induced artefacts [28]. We note that fast macroscopic movement of the synerising colloidal gels is prone to induce too low intensity in the speckle images at the gel moving edge, resulting in unreal d_2 . To check for this possible effect, a series of ΔI is added to the speckle images. The d_2 maps for different added $\Delta I = 1, 2, 5$ and 8 for the PBA gel are shown in Fig. 5.11 in the Appendix. These d_2 maps would all be flattened slightly spatially but not vary significantly between the different added ΔI , if the d_2 is real. However, our data show otherwise. With increasing ΔI , the bright stripe with high d_2 , indicating high mobility at the sample moving edge, vanishes and a stripe with low mobility (low d_2) developed, which indicates that the high d_2 is indeed artificial. This may be related to incomplete randomization of photons in this area due to the fast macroscopic movement. Therefore, all calculations and analysis in this chapter are based on speckle images masked 0.094 mm away from the sample moving edge.

To achieve calculation of $\langle \Delta r^2(\tau) \rangle$, d_2 is first converted into the electric field correlation function, g_1 , according to $g_1(\tau) = \sqrt{1 - d_2(\tau)/2\beta}$. This is based on the Siegert relation that, $g_1(\tau) = \sqrt{[g_2(\tau) - 1]/\beta}$ and the fact that $d_2(\tau) \approx 2[g_2(\tau = 0) - g_2(\tau)]$ [29]. β is the spatial coherence factor, accounting for the number of speckles detected. In the ideal case, when fluctuations of only a single speckle are detected in each pixel, β equals 1 [30]. Due to the limitations in camera-based detection, $\beta < 1$. Here β is determined such that $g_2(\tau) - 1 \rightarrow \beta$ for $\tau \rightarrow 0$. The mean square displacement, $\langle \Delta r^2(t, \tau) \rangle$, can then be extracted based on:

$$g_1(\tau) = \exp[-\gamma k_0 \sqrt{\langle \Delta r^2(\tau) \rangle}] \quad (5.2)$$

where $k_0 = 2\pi n/\lambda$ is the wave vector, with n , being the refractive index of water, λ , being the wavelength of the impinging coherent light and γ is a numer-

Figure 5.11: Time-lapse d_2 maps of PBA gel, $\tau=0.125$ s, calculated from $\Delta I = 1, 2, 5$ and 8 to the speckle images, colormap inferno. Left end of d_2 maps represents the capillary wall. Region of interest with low intensity at the moving edge of the gels is marked with the white rectangles for $t = 11$ min.

ical prefactor that is obtained from literature to be 1.5 [34, 15, 28].

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Appendix

Low Intensity Check at the Moving Edge

Fast macroscopic movement of the colloidal gels during syneresis might generate unreal d_2 values at the moving edge due to the low intensity there in the speckle images. A series of ΔI is added to the speckle images to check for this possible effect. The d_2 images for different added $\Delta I = 1, 2, 5$ and 8 for the PBA gel are shown in Fig. 5.11 in the Appendix. Region of interest, the sharp stripe at the moving edge, is marked with white rectangles for 11 min. With increasing ΔI , the bright stripe, indicating high mobility at the sample moving edge, vanishes and a stripe with low mobility developed.

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CHAPTER 6

General Discussion

This thesis aimed to understand the physical mechanisms governing syneresis, a mechanical failure that occurs in colloid-based soft solids. In the previous chapters, we addressed the research question by designing insightful experiments to disentangle, envisage and quantify the colloidal particle dynamics at multiple length scales in various colloidal materials. In this final chapter, we look back at our findings, link them together and place them in a wider scientific context. We also look beyond, delineating how these findings can pave the ways for further research and applications.

6.1 Stress Matters in Syneresis

The key word in this thesis is “syneresis”, i.e. the contraction of a material leading to the expulsion of fluid, while the material itself does not necessarily undergo a solid-to-liquid transition [1, 2]. In Chapter 3, 4 and 5, we looked into syneresis occurring in model colloidal gels and model food colloids. Colloidal gels are soft solids in which attractions between dispersed colloidal particles drive a thermodynamic instability that promotes aggregation, arriving at a space-spanning network structure of which unique mechanical and transport properties can be suitably tuned [3, 4]. During the formation of a colloidal gel, the tendency to minimize interfacial energy triggers inhomogeneous local shrinkage in the gel, which leads to random regions of higher deformation. Because the gel is elastic, there is a displacement field around each of these deformations. These inhomogeneities can then be regarded as internal stresses in the network, which can lead to macroscopic compaction [5, 6]. On top of these internal stresses, syneresis can

be triggered by external stresses, for instance, hydrostatic pressure in the “scoop” scenario in model low-fat mayonnaise. One of our aims is to obtain a deeper insight into understanding the role of the different internal and external stresses on syneresis.

In Chapter 4 and Chapter 5 we have developed methods to quantify syneresis from the stress perspective. Previous work focused mostly on quantifying the magnitude of the dimensional change of the material (L/L_0) and the volume of the expelled fluid [7], without explicitly investigating the role of the various stresses. Our results, however, show that it is the stress within the material and the spatial dependence (and heterogeneity) of that stress that matters.

In Chapter 3, we recorded the syneresis process in a colloidal gel formed via temperature-triggered adhesive forces between the particles, induced by a thermoresponsive surfactant. By forming the gel in a non-adhesive container *in situ*, syneresis is induced by endogenous contractile tension generated by the gel network itself. To first order, a poroelastic relaxation process with a rate that is limited by the fluid flow through the elastic porous material gives a good description of the kinetics of our observed syneresis process. Interestingly, we found that this relaxation process has a characteristic time scale τ that decreases with increasing initial volume fraction as $\tau \sim \phi_0^{-1}$. We hypothesize that this is due to an increase of the driving force of syneresis, i.e the internal stress, with increasing volume fraction (comparable to an increasing g in the case of gravity-driven compaction). Simulation work on syneresis of colloidal gels, with the possibility to directly calculate the local internal stress, would be valuable in elucidating this [8].

The above description, however, assumes that the permeability is homogeneous throughout the entire sample. In Chapter 5, we applied Laser Speckle Imaging (LSI) to the same system in a non-adhesive capillary, which allows us to probe dynamics during syneresis in colloidal gels that are typically turbid. We measured spatial maps of the dynamics during syneresis. Due to the rapid evolution of the material during syneresis, it is challenging to quantify the local stress from the local dynamics obtained by LSI based on microrheology concepts. Nevertheless, the spatial dependence of the dynamics does indicate that syneresis is a heterogeneous process, and suggests spatial variations in the local stress, which

are not taken into account in macroscopic measurements of syneresis, including our simplistic poroelastic model mentioned above. In this study, contributions of the gravitational stress on syneresis have been left out considering the small thickness of the capillary. A follow-up study which converts our set-up to a vertical one can investigate how hydrostatic pressure might rewrite the dynamic maps during syneresis, which would be very valuable since syneresis typically ensues after a hydrostatic pressure difference is created in consumer products.

In Chapter 4, we quantified non-accelerated syneresis in colloid polymer mixtures like low-fat mayonnaise, while systematically varying the hydrostatic pressure. We find the flow rate of expelled fluid to be proportional to the difference in hydrostatic pressure over the system. Kinetics in such syneresis can be characterized as a gravity-driven flow of the continuous phase through a densely packed region of particles, which can be described by a 1D-model based on Darcy's law, taking the geometry of the flow field into account. However, to achieve measurable expelled fluid within a reasonable measuring period, the model low-fat mayonnaise we used in Chapter 4 did yield under the smallest hydrostatic pressure we investigated. It would be insightful to look at the effect of yield stress on the expulsion flow rate in the same geometry. When yield stress is of sufficient magnitude to keep the emulsion from flowing as a whole, oil droplets might undergo compaction while remaining as a colloidal gel, instead of accumulating near the filter paper and form a compacted zone of densely packed droplets. We, therefore, speculate that permeability would be set by the mesh size of the colloidal gel, which could differ significantly from that around random close packing, $\phi_{rcp} \approx 0.64$.

Besides the stresses discussed above, surface forces, such as adhesion to container walls, matter in syneresis. In our model colloidal gel in a non-adhesive chamber described above, it is the aforementioned inhomogeneous internal stress built up during gel formation that causes the gel to shrink spontaneously and continuously with time. However, in real-life colloidal gels, like curd formed during cheese manufacturing and yoghurt, there is no macroscopic shrinkage occurring unless the material is disturbed by cutting or scooping. The key difference between these two systems is adhesion to the container walls, which prevents macroscopic shrinking in the food examples before a physical disturbance.

Coincidentally, the importance of adhesion to the container wall has been noticed in batch sedimentation experiments of particulate gels; whether there is wall slip or not depends on factors such as roughness of the wall surface, softness of the particle and attraction strength between the particles [9, 10]. Additionally, acknowledgement of the role of adhesion in syneresis raises questions on quantifying syneresis with accelerated methods like centrifugation, whereby not all the forces participating in this delicate force balance are accelerated equally [11, 12, 13]. Moreover, whether there is adhesion to the container wall during gelation might affect the endogenous stress magnitude and distribution in the gel. In the food systems mentioned above, syneresis can still occur when the sample is disturbed, i.e. when the force balance is broken. However, the timescale over which the process happens may be very different compared to the spontaneous process observed in colloidal gels formed without wall adhesion.

6.2 Solid Particles vs Liquid Particles

As introduced in Chapter 1, colloids are a state of matter ubiquitous in everyday life; they constitute most of the foods we eat, coatings we use and organs we have. The nature of the constituent particles in these systems varies from rigid, solid particles, to liquid droplets. Interestingly, syneresis is observed mostly in colloidal materials formed by droplets. We thus ask the question whether the distinct intrinsic physical properties between liquid and solid particles play a role in stress relaxation modes, which govern the apparent difference in observed syneresis. In contrast to solid particles, liquid particles can be deformed under stress and their interface is mobile. To investigate how this different particle nature influences stress relaxation, we have looked into dynamics at multiple length scales during syneresis in colloidal materials.

At the individual particle scale, there are significant differences between gels formed by liquid droplet and solid particles. In Chapter 2, we found that the mobility of individual particles depends much less on their coordination number (i.e. the number of bonded neighbours) for liquid particles than for solid particles, even though our droplets had a much higher attractive strength [14]. A solid particle within a colloidal gel can only move when all the bonds with

its nearest neighbours rupture simultaneously [15]. By contrast, liquid particles can move more easily, probably because they can slide past each other without rupturing all the bonds.

In Chapter 3, we revealed that the nature of the colloidal particle composing colloidal gels, whether they be liquid, solid, or rubbery, defines their magnitude of syneresis; the magnitude of the syneresis is greatest for particles with high interfacial mobility, i.e. droplets and rubber, and hindered for solid particles, while being still appreciable. Zooming into the mesoscopic (strand) scale, we recorded syneresis of colloidal gels comprising of droplet and solid particles as a quasi-2D layer in a PEM-coated microfluidics chamber. Particle Image Velocimetry (PIV) qualitatively unravels differences in the rearrangements that occur in the two types of gels during syneresis; in the droplet-based gels, the contraction is more uniform than in gels formed by solid particles. Due to the smooth and mobile surface, which permits lateral surfactant diffusion, individual droplets can slide relative to one another with near zero free energy cost, hence there is no bending stiffness and the resultant gels can only bear stress by stretching inter-particle bonds; this reduces the elasticity of these gels and leads to a higher extent of syneresis. By contrast, solid particle gels with a low surface mobility arrest at lower volume fraction. The rotational constraint between solid colloids generates additional bending moments that resist deformation. Indeed, we could relate these different relaxation modes of colloidal gels during syneresis to the scaling of the elastic modulus $G' \sim \phi^\nu$, where the exponent ν differs depending on the mode of stress bearing, bending or stretching of individual particle-particle bonds [16, 17].

On a macroscopic scale, we visualized for the first time the different spatial dependence during syneresis between solid and liquid particle based colloidal gels in Chapter 5. Colloidal gels consisting of solid particles exhibit a smooth decay in mobility from the moving edge into the bulk of the gel, while in droplet-composed colloidal gels, a band with high mobility developed in the bulk of the gels. We speculate that this distinct spatial dependence is a manifestation of the different relaxation modes at the strand level.

Our data clearly indicate the pivotal role of surface mobility and roughness in determining dynamics at different length scales during syneresis, deciding the

relaxation modes and ultimately, the material's fate under stress. While syneresis is more readily seen in liquid particle gels, most relevant for foods, we have shown that it is still not negligible in gels composed of solid particles. Even when no macroscopic shrinkage is observed, local syneresis may still occur during the inevitable compaction of colloidal gels without a necessity for bond breaking events and particle reattachments like in coarsening. Differences between solid and liquid particle gels have also been observed by others, for example during delayed collapse, which occurs much more rapidly and to a larger extent for liquid than for solid particles [18, 19]. Together, this calls for a revision of the current models for colloidal gel mechanics under stress, to take surface mobility and roughness into account, to reach a universal description of the relaxation mechanisms of inhomogeneous soft solids with a hierarchical microstructure.

In the following paragraphs in this section, we discuss the effects of surface roughness in colloidal systems. Particle surface roughness can lead to interlocking and an effective rotational friction between two particles [20]. Friction is a well-known parameter in determining mechanics in the granular world. For instance, it drives a shear rate induced arrest known as discontinuous shear thickening [21, 22, 23], where the viscosity of a dense granular suspension increases rapidly at a critical shear rate as the suspension reaches a jammed state. In the colloidal world, a similar link has been made between friction and a discontinuous shear thickening transition as well (Fig. 6.1 (a)) [20]. While there is sustained attention for the pronounced effects of friction in dense, sheared and repulsive systems experimentally, the role of friction in the mechanics of attractive colloidal systems has been largely overlooked.

Experimentally, in Chapter 2, we have fabricated a refractive index and density matched monodispersed droplet based colloidal system that enables in-depth studies in 3D, utilizing confocal microscopy. To further interrogate the importance of surface mobility-assisted relative sliding between particles, interfacial fluorescence recovery after photobleaching (FRAP) is a potential method [24]. To explain how such an experiment would occur; first, particles with a fluorescently labeled surfactant are prepared, which are dispersed in a refractive index and density matched continuous phase to reduce scattering for fluorescence microscopy and to be free from gravitational stress, respectively. Attractive in-

Figure 6.1: (a) Shear thickening for smooth (black) and frictional colloidal raspberry particles of, from left to right, decreasing roughness, at a constant volume fraction. For the rough particles a sudden increase in viscosity η is observed with increasing shear rate. Reprinted with permission from [20]. (b) Electron microscopy images of raspberry colloids with different roughness. Scale bar represents 500 nm. Reprinted with permission from [20]. (c-d) Schematic illustration of FRAP experiment with a colloidal gel.

teraction can be induced by depletion via adding non-adsorbing polymer. After the formation of a colloidal gel, a small region of the colloidal gel is irreversibly photobleached using high laser power, followed by monitoring the subsequent movement of the surrounding non-bleached fluorescent molecules into the photobleached region using low laser power, illustrated in Fig. 6.1 (c,d). This test would allow us to probe the sliding recovery modes at strand level in colloidal gels comprising of particles of different surface roughness. Poly(methyl methacrylate)(PMMA) [25, 14] and our polybutylacrylate (PBA) based systems in Chapter 2 can be used for comparison between solid and liquid particles. We

expect a faster fluorescence recovery for the droplet colloidal gel than for solid particle gels due to higher relative sliding. Furthermore, to zoom in on the effect of surface mobility in the liquid particle regime, colloidal gels comprising of monodispersed droplets with different viscosity can be used to fine tune the surface mobility. To study the effect of surface roughness and friction on syneresis, colloidal gels can be made that consist of “raspberry colloids” with tunable surface roughness, obtained by varying berry size and the thickness of the smoothing layer [20] (Fig. 6.1 (b)), or solid particles with attached polymers at different grafting densities. Taking the FRAP measurement to a more challenging level, instead of monitoring of particle level turn over, fluorescence recovery of a partially bleached droplet in a colloidal gel can be quantified, which can be applied to investigate surface mobility of droplets in colloidal gels formed under different attraction strength at individual particle level. Varying the attraction strength leads to different extents of deformation of the constituent droplets and different contact areas, which may result, ultimately, in different surface mobility.

Besides FRAP being a useful technique for probing local dynamics, particle locating and tracking, as we applied in Chapter 2, can provide valuable quantitative information on structural changes that occur in the gel during syneresis. To do this, the particles in the quasi-2D microfluidic, non-adhesive chamber we used in Chapter 3 can be substituted with fluorescent particles in the same set-up, to enable monitoring the colloidal gels with fluorescent confocal microscopy during syneresis. Because the turbidity of the samples is rather high, it is important to create colloidal gels that are not much more than $10\text{ }\mu\text{m}$ thick to guarantee visibility. Three-dimensional image stacks can be obtained with high-speed confocal microscopy to capture the fast dynamics during syneresis of colloidal gels. By locating and tracking the particles using previously developed algorithms [26], changes in coordination number or mean-squared displacement of the particles can be measured at individual-particle level, from which bond forming and breaking events can be counted and changes in strand length and strand tortuosity can be computed. With this information, we can probe strand buckling, bending, or sliding during syneresis.

Looking beyond macroscopic syneresis, surface mobility and roughness can manifest in different aspects of colloidal gels, for instance, the emergence of

Figure 6.2: Sketch of the dilute (a) and dense (b) path to mechanically stable gels; isostatic particles are shown in purple; non-isostatic particles are in gray. (c) Detail of a reconstruction from confocal coordinates around the percolation time in a dilute sample ($\phi = 0.08$, $c_p = 1.5$ mg/g). Isostatic particles are drawn to scale; non-isostatic ones are drawn smaller for clarity. The bond network is displayed in orange. (d) Breakup of the network by internal stress; (upper panel) reconstruction from experimental coordinates ($\phi = 0.29$, $c_p = 0.7$ mg/g) of a strand rupture event. Particles are drawn to scale and colored by a measure of two fold symmetry q_2 from blue (low) to red (high). q_2 is considered as a measure of the degree of local stretching. Reprinted with permission from [6].

mechanical metastability. Experimental studies following the kinetic process during gelation with individual-particle resolution spatially and temporally evidenced that the rigidity of colloidal gels emerges coincidentally with the isotropic percolation of isostatic particles [6]. Two distinct pathways to achieve rigidity during gelation were observed for dilute and concentrated systems, respectively, as illustrated in Fig. 6.2. For a dilute system, compact isostatic clusters form first, which are linked by non-isostatic bridges. Subsequently, percolation of isostaticity proceeds by the compaction of the floppy bridges, which requires no addition of new particles but only the local creation of new bonds at the bridge, as shown in Fig. 6.2 (a,c). In the dense regime, all particles first achieve directional percolation, followed by the growth of isostatic configurations as the number of nearest neighbors increases for the purpose of minimizing interfacial energy cost (see Fig. 6.2 (b)). During this process, the augmenting internal mechanical tension in the network results in network coarsening accompanying bond breakage, as depicted in Fig. 6.2 (d). Introducing surface mobility to the system by substituting the solid particles with droplets might alter the competition between the yield stress of the isostatic network and the internal stresses that tend to shrink the network, thus changing the mechanical metastability in colloidal gels.

Our experimental work suggests that interparticle friction plays an important role in syneresis of colloidal networks. However, in most simulation works on the mechanics of colloidal gels, friction is left out of the picture as friction is believed to be negligible at the colloidal scale due to the constant thermal vibration of particles. Therefore, our work challenges the assumption that friction can always be neglected at the colloidal scale. Interestingly, simulations on colloidal gels in which interaction between particles is described by an attractive two-body potential do not undergo syneresis. This suggests that, to understand the process of syneresis, i.e. the contraction of a colloidal network, additional particle interaction should be considered. We can find a first step in the right direction in a simulation study on coarse grained colloidal gels, where the particle-particle interaction is described by an effective interaction that includes a three-body term. There it evidences that under shear deformation, the gel experiences a negative stress normal to the shear direction, hence it would contract if volume changes were allowed in the simulations [30]. Meanwhile, with

Figure 6.3: Time evolution of (a) the average number of nearest neighbors per particle Z , (b) the structure factors $S(q)$ of the final configuration of the gel. Reprinted with permission from [27]. (c) Schematic comparing particles with homogeneous surfaces (left) and heterogeneous surfaces (right). An identical percolated structure is chosen for both particle types. (d) Osmotic pressure P normalized by $nk_B T$, where n is the particle number density, as a function of average number of bonds $\langle N_b \rangle$. The solid line is the theoretical percolation osmotic pressure using Percus-Yevick theory. (c) and (d) are reprinted with permission from [28].

the recent advances in colloidal synthesis, particles can now be tuned to be aspherical, asymmetric, or patterned [31]. This has prompted a number of particle based models for gel formation, including valence-limited and patchy-particle models [32, 33, 27, 28], and particles with anisotropic effective interactions [34, 35]. These effects constrain the relative translation and rotation of neighboring particles. By including directional attractions with sufficient valency between particles, the simulated colloidal gels are shown to have a more branched structure than the ones simulated with isotropic models. The more branched structure better resembles the experimental counterpart which is observed with con-

focal microscopy, as illustrated in Fig. 6.3 (a,b). This has been ascribed to the inhibition of lateral particle rearrangements, which strongly affect the gel topology, resulting in less coarsening of the network structure [27]. Coincidentally, surface heterogeneity of colloidal particles is evidenced to have a significant impact on the colloidal gel structure. Surface heterogeneity is introduced by surface patches with randomized functionality, as depicted in Fig. 6.3 (c). The osmotic pressure P as a function of average number of nearest neighbors $\langle N_b \rangle$ is shown in Fig. 6.3 (d). At very negative osmotic pressures, a difference emerges in $\langle N_b \rangle$ between isotropic particles ($\langle N_b \rangle = 6$) and patchy particles ($\langle N_b \rangle = 4$). These bond numbers are in concert with isostatic contact numbers of frictionless spheres ($z_{iso} = 6$) and perfect frictional spheres ($z_{iso} = 4$), respectively, implying the similarity in constraint originated from surface heterogeneity and from surface friction. Moreover, again, the network would show syneresis if it was permitted to detach from the boundaries, implied by the negative osmotic pressure [28]. Friction between multiple particles leads to an effective bending stiffness, therefore strand level dynamics needs to be taken into account to understand colloidal network mechanics. Interesting physics is to be unraveled on colloidal gel mechanics by particle-based simulations which permit syneresis and explicitly includes interparticle friction.

6.3 Colloidal Dynamics with Different Polymer

Bringing particles in a colloid into a kinetically arrested gel state imparts desirable mechanical stability for related applications. However, perfect mechanical stability can never be attained, as particles are never at true rest but continuously evolve aiming to minimize interfacial energy cost. These aging dynamics can be amplified under external load, arriving at local weak spots which grow into a global failure of the material [36]. If a gel could reach equilibrium, it would consist of two macroscopically separated phases, one with all the particles and one with no particles for typical interparticle attractions, rather than the observed colloidal gel structure. Thus, understanding these internal dynamics would improve the stabilization of the internal stresses and prevent mechanical failure like syneresis. In many manufactured food products, colloidal particles are embed-

ded in an elastic matrix, for example consisting of polymers added as thickeners, for improving handling, texture, and shelf-stability. The particle dynamics in such soft composite materials remain largely unexplored.

In Chapter 2, we looked into the internal dynamics of liquid particles, brought to an arrest state via different kinetic routes due to different architectures of the added polymer. Linear polymers lead to a depletion attraction that induces the formation of a colloidal gel, while crosslinked gel particles (Carbopol) provide background elasticity; we also added microgel particles that could both induce depletion attraction and provide elasticity. We evidenced that, while the ensemble-averaged particle dynamics in these materials are very similar, the underlying individual particle dynamics exhibit distinct features. The fact that ensemble averaging fails to capture the existing difference draws attention to interpretation of colloidal particle dynamics based on averaging data in samples with heterogeneous structures in literature. The variations in particle dynamics may lead to differences in structural rearrangement, ultimately, arriving at different responses to stress, which might prompt additional sources of heterogeneity that must be studied without averaging.

If we are to understand how the discussed dynamics are amplified with external stresses, individual particle level information of materials under deformation is required. Using the same system discussed above, we can take one step further to resolve the changes of the three-dimensional structure and particle dynamics upon repeated shear deformation. To achieve this, we developed a low-cost shear cell, which can be installed on top of a conventional inverted confocal microscope, allowing the gel to be imaged under shear with individual-particle resolution, as illustrated in Fig. 6.4 (a,b). The cell consists of a bottom plate made of a round cover slip with a metal ring glued to it to guarantee stability of the bottom plate during shear and a square glass slide functioning as the top plate. The square glass slide is placed on top of the cover slip and is then glued to a post which connects to a micrometer. This ensures that the two plates are parallel to each other. The top plate is first lifted to 50 μm higher than the designed chamber height for sample loading and is then lowered to the designed height, after which excess of the sample is trimmed. Thus, under and over sample loading can be minimized. We managed to apply cyclic shear with a strain of 1 to the

Figure 6.4: (a) Shear cell set-up; the cell consists of a bottom plate, i.e. a round cover slip (50 mm, Thermo Scientific), with a metal ring (M16, Sencys, inner diameter 16 mm, thickness 4 mm) glued to it using Norland Optical Adhesive 61UV curable glue for stability and a top plate, i.e. a square glass slide (10 mm $\times$ 10 mm). The top plate is glued to a post with M4 screw using 5 minute epoxy gel (Devcon). The post connects the cell to a micrometer head (BM11.166, Newport) which determines the gap size of the cell and a single-axis (x) translation stage with a motorized actuator (Z825B, Thorlabs) is mounted. The actuator is controlled by a K-Cube Brushed DC Servo Motor Controller (KDC101, Thorlabs), which can be controlled using Thorlabs' Kinesis software. The set-up is mounted to the microscopy stage with a base plate using screws. (b) Schematic illustration of the shear-confocal set-up with a side view. (c) Computer-generated renderings from experimentally determined particle positions for Carbopol, $c_p = 16.5$ mg/ml, $\phi = 0.25$. Averaged Z as a function of sample height for (d) Carbopol, $c_p = 16.5$ mg/ml and (e) PAA, $c_p = 16.5$ mg/ml at a constant particle volume fraction, $\phi = 0.25$.

Carbopol sample and microgel sample with a polymer concentration, $c_p = 16.5$ mg/ml. Three-dimensional particle locations were extracted from the confocal

microscopy image stacks of the initial state and after each cycle.

To begin evaluating the microstructure, we determined the coordination number, Z , for each particle by identifying all of its nearest neighbors. Particles are identified as nearest neighbors if their center-to-center distance is within a cut-off value, $2.2a$, with a being the particle radius. For both polymer architectures, we observe an inhomogeneous Z as a function of sample depth, which can be attributed to the shear induced during sample loading, as shown in Fig. 6.4 (c). To better compare the structural changes before and after cyclic shear, regardless of the sample depth dependence on Z , the average Z is computed for a $4\text{ }\mu\text{m}$ slab of the observed 3D structure for the initial state and the state after the 10th cycle, as illustrated in Fig. 6.4 (d,e). For both polymer architectures, there is a slight increase in Z after 10 cyclic shear deformations. We hypothesize that shear deformation facilitates particle escape from local energy minima and rearrange to a more energetically favorable state where there is enhanced particle contact. Quantitative analysis on properties such as dimension of the pockets, volume fraction inside the pockets and sphericity of the pockets are needed for a more complete picture of the topological changes in such soft composites under deformation. In the case where a colloidal gel is induced by adding non-adsorbing linear polymer, instead of true shear deformation, plug flow is observed due to wall slip in the current shear cell set-up. This issue has been solved in collaboration with a fellow PhD candidate, Joanne Verweij, by modifying the set-up as follows: (i) both the glass slide as the top plate and the cover glass as the bottom plate are coated with PEM; cationic and anionic layers are added alternatively for 3 layers and 2 layers, with thorough rinsing in between. (ii) The bottom plate is then coated with a single heterogeneous layer of the particles which form the colloidal gel. (iii) A TEM grid (Agar Scientific, G27 60C Hex 700 thin bar copper, 3.05 mm) is attached to the top plate with 250 μm spacers (Precision Brand, 0.254 mm). Topological analysis based on systematic measurements under shear deformation on these colloidal composites with different polymer additives and dynamics from particle location hold predictive power for the lifetime of the network as a whole.

In our study, particle mobility in the microgel sample resembles that in the Carbopol sample. However, we expect that this may depend strongly on the type

and size of the microgel particles. Therefore, it would be interesting to investigate how the properties of the microgels influence the colloidal particle dynamics; this would be highly informative to rationalize polymer addition to achieve the desired macroscopic properties in relevant soft composites. Exploring this would require microgel particles of different sizes and cross-link densities [37]. We speculate that upon decreasing the cross-link density, the particle dynamics in the composite would shift to more colloidal gel-like, as the effect of depletion attraction would become more and more pronounced while the background elasticity declines. Thus, the macroscopic properties in such soft solids could be tuned by choosing the type of microgel particle.

Conclusion & Outlook

Syneresis is a mechanical instability in which the fluid and particle dynamics involve a wide range of time and length scales. The results in this thesis have shed light on the microscopic mechanisms that govern syneresis in colloidal materials. We have gained deeper insight and understanding into different stresses and interfacial mobility that contribute to syneresis. However, it is clear that syneresis as mechanical process which leads to product instability needs further scientific attention. We hope to stimulate theoretical and experimental effort on unraveling the scientific origins of this mechanical instability for a more complete picture in understanding mechanics in colloidal materials.

Such understanding would open up many new possibilities for the rational and guided design of applications with desired mechanical properties. For instance, for food products, one of the fields where research on syneresis has been most appreciated, it would be beneficial to investigate the role that boundary conditions play in product stability against syneresis.

As shown to us by the colloidal particles with more surface mobility, it helps to relax when one is flexible!

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Summary

Soft colloidal solids are ubiquitous to life. Their stability is crucial to consumer products and the rich mechanical properties they exhibit make them valuable subjects to investigate to meet the growing demand for sustainable, high-quality materials. Upon stressing soft colloidal solids, they experience a variety of relaxation mechanisms, one being syneresis, the compaction of the material, leading to the expulsion of fluid. Syneresis displays a wealth of complex phenomena that makes its study fascinating yet challenging. In this thesis, we looked into particle dynamics during syneresis at multiple length scales in various soft colloidal materials to reveal underlying physics governing mechanics in such soft disordered solids.

In Chapter 2, we unravel the internal individual particle level dynamics of three colloid polymer mixtures where the polymer architecture is altered. We compare particle dynamics between three common ‘thickeners’, linear polymer, microgel and a subgranular gel, by creating a model colloidal system which enables fast 3D confocal microscopy. From recorded image stacks, we disentangle ensemble and individual particle dynamics based on local neighborhood and find stark differences. We utilize a common methodology of the van Hove distribution to characterize these contrasting particle dynamics between a majority of bound particles and a minority of highly mobile particles. Finally, by parameterizing these distributions, we provide an approach to distinguish separate phases which these composites resemble, namely, a colloidal gel or a colloidal glass. We believe that these findings provide not only a rich investigation of the dynamics within composite colloidal materials but also key insights into how such dynamics can manifest in widely studied macroscopic phenomena such as syneresis,

delayed failure, and coarsening.

In Chapter 3, we study how dynamics during syneresis in a colloidal gel is defined by stress relaxation at the strand level. We form *in situ* colloidal gels composed of three different types of particles with contrasting nature: liquid droplets, solid polymer, and crosslinked rubber, all with an identical averaged size. By creating the gel *in situ*, endogenous stresses which arise during network formation are not disrupted by shear during sample mixing. Crucially, the interparticle attraction is constant as it is triggered by a thermoresponsive surfactant, which leads to attraction upon heating to a fixed temperature. We find that syneresis occurs rapidly upon gelation only if the container walls are rendered non-adhesive. The magnitude of this syneresis is greatest for particles with high interfacial mobility, i.e. droplets and rubber, and hindered for solid particles, while being still appreciable. We perform microscopic and mechanical measurements to deduce that this magnitude is related to the modes of stress relaxation within the network by either the stretching of interparticle bonds or the bending of entire gel strands. While connectivity has recently received enormous attention in such heterogeneous networks, our results highlight that it is only one part that defines the network dynamics, with both boundary conditions and interfacial mobility playing equally important roles. This sheds new light on instability in soft thermal solids and calls for new theoretical descriptions of soft gel mechanics in which boundary conditions and interfacial mobility are taken into account.

In Chapter 4, we move to the dynamics during syneresis at macroscopic level. We directly quantify syneresis in colloid polymer mixtures like low-fat mayonnaise by non-accelerated observation, avoiding disproportionate acceleration of the participating forces in the force balance. We devise a new method of mimicking syneresis triggered by scooping in a controlled and reproducible manner. This allows us to investigate quantitatively the effect of the hydrostatic driving force. Furthermore, we look into the resisting osmotic pressure which is thought to play a key role in limiting syneresis. Additionally, we characterize the composition of the expelled fluid. We find that the flow rate of expelled fluid is proportional to the difference in hydrostatic pressure over the system. We conclude that syneresis is controlled by the permeability of the network and

that its kinetics can accurately be described with a 1D model based on Darcy's law by accounting for the complex geometry and microstructure. To this end, we develop a model which predicts the kinetic behaviour observed during this gravity driven syneresis. We believe that these direct measurements of syneresis over long-time periods and over a comprehensive set of experiments provides a crucial step forward, which may lead to further debate on the microstructural physical origins in soft matter and in particular food stabilization.

To date, the studies on dynamics during syneresis have left out possible heterogeneities in the material. In Chapter 5, we take the first steps to investigate spatial dependence of dynamics during syneresis experimentally. We apply the technique Laser Speckle Imaging which allows us to elucidate internal dynamics within turbid materials with high spatiotemporal resolution. Syneresis colloidal gels comprising of particles with different nature, as also studied in Chapter 3, are used here. We find that both colloidal gels exhibit heterogeneous dynamics during syneresis. Furthermore, we identify the distinct spatial dependence of dynamics in gels composing of different particles; the solid particle gel shows a smooth decay in mobility from the syneresis interface into the bulk, while the droplet based gel develops a band with high mobility a few hundred micrometers behind the interface of the sample. We hypothesize that this difference is a manifestation of the different ways in which the networks bear stress, depending on the composing particle nature. These results provide unique insights in understanding the colloidal gel mechanics from a fundamental level. Additionally, we present a proof of concept measurement with LSI on syneresis commercial food products, which opens new opportunities in investigating food stabilization in a non-invasive fashion and, ultimately contributing to predict and control the product stability.

Finally, in Chapter 6, the general discussion, we place our findings in an expanded scientific context and give an outlook for future research into and beyond syneresis in mechanics of soft disordered solids.

List of Publications

THIS DISSERTATION:

- Qimeng Wu, Melle T.J.J.M. Punter, Thomas E. Kodger, Luben Arnaudov, Bela M. Mulder, Simeon Stoyanov, and Jasper van der Gucht: **Gravity-driven Syneresis in Model Low Fat Mayonnaise** *Soft Matter*, 15(46), 9474-9481 (2019) (Chapter 4)
- Qimeng Wu, Ruben Higler, Thomas E. Kodger and Jasper van der Gucht: **Particle Dynamics in Colloid Polymer Mixtures with Different Polymer Architecture** *ACS Applied Materials & Interfaces*, 12(37), 42041–42047 (2020) (Chapter 2)
- Qimeng Wu, Thomas E. Kodger and Jasper van der Gucht: **Syneresis of Colloidal Gels: Endogenous Stress and Interfacial Mobility Drive Compaction** Accepted in *Physical Review Letters* (2020) (Chapter 3)
- Qimeng Wu, Jesse Buijs, Sanne de Groot, Thomas E. Kodger and Jasper van der Gucht: **Unravelling Spatially Heterogenous Dynamics in Colloidal Gels during Syneresis** Manuscript in preparation

OTHER WORK:

- Jielun Hu, Shaoping Nie, Qimeng Wu, Chang Li, Zhihong Fu, Joshua Gong, Steve W. Cui and Mingyong Xie: **Polysaccharide from Seeds of *Plantago asiatica* L. Affects Lipid Metabolism and Colon Microbiota of Mouse** *Journal of Agricultural and Food Chemistry* 62(1), 229-234 (2014)

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Overview of completed training activities

Discipline specific activities

CHAINS, Veldhoven (NWO, 2016)

Physical Chemistry Winterschool, Han-sur-Lesse, (BE) (WUR & TU Delft, 2017)

Advanced Soft Matter, Wageningen (2017)

Dutch Soft Matter Meeting, The Netherlands (2016-2018) †

Food Colloids, Leeds (UK) (2018)*

Rheology Workshops, Wageningen (2018)

Dutch Materials, Utrecht (4TU.HTM, 2018)

Jülich Soft Matter Days, Jülich (DE) (SoftComp, 2018)†

Physics@Veldhoven, Veldhoven (NWO, 2018-2020)†*

Microscopy and Spectroscopy in Food and Plant Sciences, Wageningen (WUR, 2019)

ACS Colloids and Surface Science Symposium, Atlanta (U.S.A) (ACS, 2019)†

†Oral presentation

*Poster presentation

General courses

VLAG PhD week, Baarlo (VLAG, 2016)

Taking charge of your PhD, Utrecht (NWO-I, 2016)

Scientific Publishing, Wageningen (WUR, 2016)

The Art of Presenting Science, Utrecht (NWO-I, 2017)

Scientific Writing, Wageningen (WUR, 2018)

Scientific Artwork, Wageningen (WUR, 2019)

Career Planning, Utrecht (NWO-I, 2019)

Masterclass on Data Visualization, Utrecht (Dutch Chemometrics Society, 2019)

Optionals

Preparation of Research Proposal (2016)

Group meetings & Colloquia (PCC, 2016-2020)

Journal Club (PCC, 2016-2020)

Soft Hybrid IPP meeting (NWO & Unilever, 2016-2020)

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