An experimental study of the jamming dynamics in suspensions of soft colloidal particles

by

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Dedicated to

My family, my friends and my teachers. Without their support, this wouldn't have been possible.

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Declaration

I hereby declare that the work presented in this thesis is completely original. This research work is carried out under the supervision of **Prof. Ranjini Bandyopad-hyay** at **Raman Research Institute, Bengaluru, India**. This dissertation is the result of my own work unless otherwise stated. No part of this thesis has been submitted elsewhere for the award of any degree, diploma, membership, fellowship or any other similar title of any university or institution. I also declare that this thesis has been passed through the **Turnitin** software to check for plagiarism.

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Certificate

This is to certify that the work contained in the thesis titled 'An experimental study of the jamming dynamics in suspensions of soft colloidal particles', submitted by Chandeshwar Misra to Jawaharlal Nehru University for the award of the degree of Doctor of Philosophy in Physical Sciences, is his original research work. The results embodied in the thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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Synopsis

Soft materials such as colloidal particles and microgels are often used as model systems to study the phase behavior and dynamics of complex materials. A colloidal suspension can show a variety of phases depending on temperature, effective volume fraction and nature of interparticle electrostatic interactions. Suspensions of soft colloidal particles can show a continuous buildup of structure in a physical aging process that arises due to a spontaneous and gradual evolution of the interparticle electrostatic interaction. Soft colloidal particles can be synthesized with tunable interaction potentials and show very interesting packing behaviors. The effects of particle softness on interparticle interactions and phase behavior have been the focus of extensive structural studies. Dense aqueous suspensions of soft colloidal particles are often used as model systems to study glass transition dynamics. In this thesis, we investigate the slowing down dynamics of soft colloidal suspensions near their jamming transitions using different experimental techniques such as dynamic light scattering, rheology, cryogenic scanning electron microscopy, etc.

Chapter 1 provides the background knowledge required to comprehend the research work presented in this thesis. This chapter gives a brief introduction to colloidal systems and contains a detailed discussion on suspensions of aging and thermoresponsive colloidal particles. We introduce colloidal interparticle interactions such as van der Waals interaction and screened electrostatic repulsion. A detailed description of the swelling, exfoliation and structure formation processes in aging colloidal smectite (Laponite[®]) clay suspensions is next presented. The aging dynamics and phase behavior of aqueous Laponite suspensions are discussed in detail. The chapter concludes with discussions on the jamming dynamics of colloidal suspensions and the rheological behaviors of aging clay suspensions and thermoresponsive microgels.

Chapter 2 describes sample preparation methods and experimental techniques used in this thesis work. A detailed description of the synthesis methods used to control the size and stiffness of thermoresponsive colloidal particles is given here. Thermoresponsive microgels of different stiffnesses are synthesized by varying the concentration of the crosslinkers in the one-pot synthesis method. The experimental techniques employed in this thesis include dynamic light scattering, rheological measurements, scanning electron microscopy (SEM), cryogenic SEM, differential scanning calorimetry and dielectric spectroscopy. Each of these techniques and the methods of data analysis are discussed in this chapter.

In chapter 3, we study the competitive effects of solvent structures and interparticle electrostatic interactions on the aging dynamics and rheology of aqueous suspensions of a colloidal smectite (Laponite) clay. We perform dynamic light scattering (DLS) and rheological experiments to investigate the changes in suspension dynamics when different additive molecules, both dissociating and non-dissociating molecules, are incorporated in the medium. The addition of glucose enhances hydrogen bonding in water, increases osmotic pressure gradients and results in accelerated suspension aging. The presence of N,N-Dimethylformamide in water, on the other hand, disrupts hydrogen bonding, reduces osmotic pressure gradients and suppresses suspension aging. Salts such as sodium chloride and potassium chloride dissociate into ions when added to water, while also locally altering water structure. Laponite suspensions in the presence of dissociating salts show accelerated kinetic arrest, which is attributed to the dominance of electrostatic interactions over changes in solvent structure. Rheological experiments, performed to study the effects of the solvent structure and interparticle electrostatic attractions on the aging dynamics of aqueous Laponite suspensions, verify the results of our DLS experiments. We observe that the microscopic dynamics of aging Laponite suspensions show selfsimilar time-evolution, while their nonlinear rheological responses are sensitive to the presence of additive molecules. Finally, we perform cryogenic scanning electron microscopy experiments to correlate the microstructures of the suspensions with their aging dynamics and rheology. Our study highlights that solvent structure is a key parameter in determining the dynamics and rheology of suspensions of smectite clay colloids. On the other hand, electrostatic interparticle attractions induced by dissociating additive molecules dominate over changes in solvent structure in determining the aging dynamics of the suspensions.

Chapter 4 describes the role of different thermal histories on the aging dynamics of aqueous Laponite suspensions. These experiments are performed following two different protocols. In the first protocol, the temperature of the solvent is set before the addition of Laponite powder and is maintained throughout the stirring time (45 min). We label these as prefixing experiments. In contrast, in the second protocol, the temperature of the suspension is set after stirring of the sample is stopped. We label these as postfixing experiments. We observe an enhancement in the suspension aging dynamics with an increase in temperature. We explain this observation by considering an increase in the dissociation of Na⁺ from the Laponite platelets. While an increase in temperature is expected to disrupt the hydrogen bonding in the medium, an enhancement in the interparticle electrostatic attraction, arising due to dissociation of Na⁺ from the Laponite platelets, dominates over any effect that alteration of solvent structure may have on the suspension dynamics. When compared to experiments in which temperature of the suspension is changed after the addition of Laponite (postfixed case), we observe enhancements in the dissociation of Na⁺ and suspension aging dynamics when the solvent temperature is raised before the addition of Laponite particles (prefixing experiments). The microscopic aging dynamics show self-similar behavior irrespective of suspension temperature histories.

Chapter 5 describes the influence of particle size on the thermoresponsive and rheological properties of aqueous poly(N-isopropylacrylamide) (PNIPAM) colloidal suspensions. PNIPAM particles of different sizes are synthesized by varying the concentration of sodium dodecyl sulfate (SDS) in a one-pot synthesis method. The sizes, size polydispersities and the thermoresponsivity of the PNIPAM particles in aqueous suspensions are characterized by using dynamic light scattering and scanning electron microscopy. The lower critical solution temperature (LCST) of suspensions of these particles are characterized using differential scanning calorimetry. We observe a decrease in the sizes of these particles with an increase in SDS concentration. In this study, we show that the stiffness of PNIPAM particles can also be controlled by varying the SDS concentrations. The stiffness of these particles is characterized in terms of their maximum swelling ratios. The maximum swelling ratio α of PNIPAM particles in aqueous suspensions, measured from the thermoresponsive curves, is defined as $d_{20^{\circ}C}/d_{50^{\circ}C}$ $(d_{fullswell}/d_{fullshrunk})$, $d_{20^{\circ}C}$ and $d_{50^{\circ}C}$ refer to the hydrodynamic diameters of the particles at 20° and 50°C ($d_{fullswell}$ and $d_{fullshrunk}$) respectively. The maximum swelling ratios of PNIPAM particles are observed to increase with a decrease in particle size. This observation is understood by minimizing the Helmholtz free energy of the system with respect to the swelling ratio of the particles. Finally, we investigate the dynamics of these particles in jammed aqueous suspensions by performing rheological measurements. The viscoelastic moduli of aqueous suspensions of these particles at an identical effective volume fraction, measured from temperature sweep rheological experiments, are observe to increase with a decrease in swelling ratios at a temperature below the LCST. We observe a non-monotonic behavior in both the moduli with an increase in temperature.

In chapter 6, we study the phase behavior and mechanical response of aqueous suspensions of PNIPAM colloidal particles of different stiffnesses and at different suspension temperatures. The stiffness of the PNIPAM particles is characterized by their maximum swelling ratios. With increasing temperature, dense suspensions of PNIPAM particles show a non-monotonic variation in viscoelastic moduli. We observe that the elasticity of the sample increases when the temperature of aqueous suspensions of these particles is increased above the lower critical solution temperature (LCST). The observed increase in viscoelastic moduli above the LCST is explained by considering that the hydrophobicity of the particles increases with temperature. We perform Fourier transform infrared (FTIR) spectroscopy experiments to measure the hydrophobicity of PNIPAM particles of different swelling ratios and at different suspension temperatures. From rheological experiments, we note that PNIPAM suspensions of soft particles are less elastic when compared to suspensions of stiff particles. Since changes in temperature and particle stiffness are expected to affect the underlying microscopic structures of dense suspensions of these particles, we directly visualize the suspension structures using cryogenic scanning electron microscopy experiments at temperatures below and above the LCST and for different particle stiffnesses.

Chapter 7 describes the effects of applied oscillatory shear stresses on the dielectric properties of dense aqueous suspensions of PNIPAM particles at different temperatures. In these experiments, we use a rheometer to apply a constant oscillatory strain and simultaneously measure the dielectric response of the sample using an precision impedance analyzer. We observe a decrease in dielectric parameters such as dielectric permittivity and dielectric loss with an increase in the applied oscillatory strain. In contrast, we observe an increase in the dielectric parameters when the temperature of the sample is increased. When compared to suspensions at temperatures below the LCST, the dielectric properties of dense aqueous suspensions of PNIPAM particles at higher temperatures (near and above LCST) are insensitive to changes in the amplitude of the applied oscillatory strain. This can be attributed to the breakdown of suspension structures, formed by PNIPAM particles in dense suspensions below the LCST, due to the application of the oscillatory strain. Our rheo-dielectric experiments, which allow us to study the material's properties over a length scale range varying several (7–8) orders of magnitude, reveals that the dynamics of PNIPAM particles in suspensions slow down at smaller length scales (nanometers) under large oscillatory deformations. In contrast, dynamics of the same suspensions accelerate with applied deformation (shear thinning) at macroscopic length scales.

In chapter 8, we study the dynamics of suspensions of thermoresponsive coreshell colloidal particles approaching a kinetically arrested state. We synthesize shell monomers (NNPAM) using Schotten-Baumann reaction and use a magnetic resonance spectroscopy technique to confirm the presence of the amide group. Next, using a two-step synthesis protocol, we synthesize core-shell particles with shells composed of poly(*N*-n-propylacrylamide) (PNNPAM) with LCST of 21°C and cores consisting of poly(n-iso-propylmethacrylamide) (PNIPMAM) of LCST 44°C. The combination of distinct monomers that form the core and shell of the particle results in a microgel with extraordinary linear swelling properties. The linear swelling property is produced because of the large gap of 23°C between the LCTSs of the core and shell-forming polymers. In our rheological experiments with dense aqueous suspensions of these particles, we observe three-step changes in the viscoelastic moduli with increase in suspension temperature. The observed variation in the viscoelastic moduli with temperature is attributed to the linear swelling properties of core-shell particles arising from the large LCST gap. Finally, we perform large amplitude oscillatory shear (LAOS) experiments of dense suspensions of core-shell particles.

Chapter 9 describes the effects of stiffness of the core particles on the rheological behavior of dense aqueous suspensions of core-shell thermoresponsive colloidal particles. We perform oscillatory temperature sweep and strain amplitude sweep experiments to study the flow behaviors of dense aqueous suspensions of core-shell particles, with the core particles characterized by different stiffnesses. We observe that the elasticities of samples of identical effective volume fractions increase with increasing stiffnesses of the core particles. Finally, we perform large amplitude oscillatory shear (LAOS) experiments of dense suspensions of core-shell particles with different core stiffnesses to study the non-linear rheological properties of these suspensions.

Chapter 10 summarizes the main results of this thesis and briefly discusses the scope for future work.

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List of Publications

Publications included in the thesis

- Influence of particle size on the thermoresponsive and rheological properties of aqueous poly(*N*-isopropylacrylamide) colloidal suspensions
 Chandeshwar Misra, Sanjay Kumar Behera and Ranjini Bandyopadhyay. Bulletin of Materials Science, 43, 182, 2020.
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- Influence of medium structure on the physicochemical properties of aging colloidal dispersions investigated using the synthetic clay Laponite Chandeshwar Misra, Venketesh T. Ranganathan and Ranjini Bandyopadhyay. Soft Matter, 17, 9387-9398, 2021. DOI: 10.1039/D1SM00987G
- Dichotomous behaviors of stress and dielectric relaxations in dense suspensions of swollen thermoreversible hydrogel microparticles
 Chandeshwar Misra, Paramesh Gadige and Ranjini Bandyopadhyay.
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- 4. Hydrogel stiffness determines particle self-assembly and suspension rheology across the lower consolute solution temperature Chandeshwar Misra, Sanjay Kumar Behera and Ranjini Bandyopadhyay. Under review in *Journal of Chemical Physics*. Arxiv link - https://arxiv.org/pdf/2210.09694.pdf

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Chapter 1

Introduction

1.1 Colloidal suspensions

Colloidal suspensions are heterogeneous systems in which particles of solid or droplets of liquid or gas are dispersed in a continuous medium [1]. The sizes of colloidal particles can range from 10 nm -1 μ m [2]. The lower limit comes from the requirement that the dispersed particles be significantly larger than the molecules of the suspension medium. The upper limit ensures that the particle's Brownian motion is not dominated by external effects such as gravitational settling or convection. A colloidal system can be categorized depending on the suspension medium and dispersed phase. Very familiar examples of colloidal systems are foams (gas in liquid), milk (liquid in liquid), ink (solid in liquid), smoke (solid in gas), ruby glass (solid in solid), paints (solid in liquid), etc. [3–5]. Due to the small sizes of colloidal particles, thermal fluctuations are highly relevant. As a consequence of collisions with molecules in the suspending medium, colloidal particles undergo random movement called Brownian motion, which can be observed in experiments [6]. The thermal energy of a colloidal particles is of the order of k_BT , where k_B and T are the Boltzmann constant and suspension temperature, respectively.

1.2 Interparticle interactions in colloids

The nature of interparticle forces acting between colloidal particles plays an important role in determining their microscopic organization and stability in suspension [7]. The interparticle potential has the simplest form for suspensions of hard colloidal particles. The interparticle interaction potential of hard sphere colloids in suspension is given by $V(r) = \infty$ for $r \leq \sigma$ and V(r) = 0 for $r > \sigma$ [1]. Here, r is the distance between the centers of the two interacting spherical particles and σ is the sum of their radii. A dilute colloidal suspension of hard spheres has no potential energy and the dynamics are solely governed by the particles' volume fraction ϕ . However, the dynamics of dense colloidal suspensions consisting of charged particles are regulated by the various interactions acting between them, such as electrostatic repulsion, van der Waals and hydrophobic attractions [8, 9].

1.2.1 Electrostatic repulsions

Colloidal particles are characterized by several features such as surface adsorption of surfactants [10, 11], isomorphous substitution [12–14], and ionic exchange [15, 16]. The surface charge of colloidal particles is balanced by equal and oppositely charged ions, which are called counterions. Some of the counterions are tightly bonded to the colloidal surface. The layer close to the colloidal surface including these counterions is known as the Stern layer [17] (figure 1.1). The other counterions form a diffuse atmosphere of ions close to the colloidal surface. The counterions remain in a diffused state within a layer around the charged particle due to thermal fluctuation and screen the charged particle surface. The counterion concentration decreases with distance from the surface of the colloidal particle. This diffuse layer of counterions, together with the surface charges, form the electric double layer (EDL) [1] (figure 1.1). When two colloidal particles approach each other, the overlap of their double layers causes an electrostatic repulsion which can stabilize the particles against aggregation. This is known as electric double layer repulsion. The effect of the interaction due to



Figure 1.1: Schematic diagram of the electric double layer (EDL) of a negatively charged colloidal particle in suspension. This figure is adapted from www.substech.com.

double layer repulsion between two colloidal particles is experienced over a distance given by the Debye screening length $(1/\kappa)$. The Debye screening length measures the range of the electric potential that extends from the surface of charged colloids and depends on the electrolyte concentration in the suspension. It is given by the following expression [18].

$$\frac{1}{\kappa} = \left[\frac{\epsilon_0 \epsilon_r k_B T}{\sum_i (z_i e)^2 n_i}\right]^{1/2} \tag{1.1}$$

Here, ϵ_0 is the permittivity of vacuum, ϵ_r is the relative permittivity of the medium, k_B is the Boltzmann constant, T is the suspension temperature, e is the charge of an electron and z_i is the valency of *i*th ion species of concentration n_i .

When a colloidal particle moves in the suspension medium, a layer of the surrounding liquid remains attached to the particle and remains stationary. The boundary of this surface is called the slipping plane (shear plane). The value of the electric potential up to this plane is known as the zeta potential [1, 7, 17]. Since it is challenging to measure the exact potential at the surface of a colloidal particle, the zeta potential at the slipping plane can be used to estimate the charge on the colloidal surface. As a good approximation, the zeta potential can be considered as the potential at the Stern layer.

The free energy per unit area W_{DL} between two charged plates placed at distance 2d can be written as a function of d [1, 17]:

$$W_{DL}(d) = \left(\frac{64nk_BT}{\kappa}\right)\gamma^2 e^{-2\kappa d}$$
(1.2)

where *n* is the number density and $\gamma = tanh(ze\Phi_0/4k_BT)$, *z* is the valency of the counterions and Φ_0 is the surface electric potential. The interaction between two colloidal particles surrounded by Debye layers can be approximated by equation 1.2.

1.2.2 van der Waals attractions

The van der Waals interactions are attractive in nature. All atoms and molecules can experience van der Waals interactions [19]. Generally, two atoms with permanent dipole moments can attract each other via dipole-dipole interactions [20]. Neutral atoms and molecules, however, can be thought of as rapidly fluctuating dipoles due to the rapid motion of electrons around their nuclei. As the dipoles couple with each other, London dispersion interactions minimize the energy of interaction [1, 21]. As colloidal particles are composed of many molecules, the London dispersion interaction manifests as the attractive van der Waals force between two colloidal particles [22]. The effective range of this van der Waals attraction can vary from 0.1 nm to 10 nm [23]. The strength of the van der Waals interaction depends on the dielectric properties of the colloidal particle and suspension medium.

For two parallel plate systems, which is an approximately correct description of the aging clay nano-platelets that are investigated in this thesis, the van der Waals interaction energy is given as follows [17, 24]:

$$W_{\nu dW(d)} = -\frac{A}{48\pi} \left[\frac{1}{d} + \frac{1}{(d+\delta)} - \frac{2}{(d+\delta/2)} \right]$$
(1.3)

where, d, δ and A are the half distance between two plates, the thickness of the plates and Hamaker constant (1.06 $\times 10^{-20}$ J [22]) respectively.

1.2.3 Hydrophobic interactions

Water molecules form robust and intermolecular hydrogen bonds. As a result of hydrogen bonding, pure liquid water forms a highly ordered network. Non-polar or hydrophobic molecules such as alkanes, hydrocarbons, fluorocarbons, inert atoms, etc. are incapable of forming hydrogen bonds with water molecules. When hydrophobic molecules are added to water, the surrounding water molecules try to reorient themselves to form an ordered structure around the hydrophobic molecules. This reorientation or restructuring of water molecules around a hydrophobic solute is entropically very unfavorable since it imposes a new and highly ordered structure on the neighboring water molecules [18]. The hydrophobic molecules, therefore self assemble by pairwise attraction in order to minimize the free energy of the system. The attraction forces between two hydrophobic molecules were first estimated experimentally by Israelachvili and Pashley [25]. The hydrophobic attraction is much stronger than the van der Waals force and decays exponentially in the range 0-10 nm [26].



Figure 1.2: Top: Phase diagram of suspensions of monodisperse hard spheres as a function of particle volume fraction ϕ . Green solid arrows indicate equilibrium states, while dashed arrows indicate out of equilibrium states. Bottom: Confocal microscope images of the sequence of phases in a colloidal suspension with 8% particle size polydispersity. This figure is adapted from [2].

1.3 Different phases in colloidal suspensions

The dynamics, structure and mechanical behavior of colloidal suspensions can be easily studied using several experimental techniques such as light scattering, microscopy and rheology [27–31]. The phase behavior of dense colloidal suspensions was first studied experimentally by Pusey and van Megan using a nearly hard sphere colloidal system (PMMA) [32, 33]. The phase behavior of a colloidal suspension is entirely determined by excluded volume interactions between the constituent particles. Figure 1.2 represents the phase diagram of suspensions of hard spheres with polydispersity of 8% as a function of volume fraction ϕ [2]. It is noted from figure 1.2 that the suspension show a liquid state at volume fraction $\phi < 0.494$. Next, the coexistence of liquid and crystalline phases is observed when the volume fraction of the suspension is increased above $\phi = 0.494$. However, if the volume fraction of the suspension is increased rapidly, a supercooled phase is observed for volume fractions $0.494 < \phi < 0.58$. The suspension displays a glassy phase between volume fractions $0.58 < \phi < 0.64$ (ϕ_{rcp}). Here, $\phi_{rcp} (\approx 0.64$) is the maximum volume fraction for the random close packing of hard spheres, and its value depends on the size polydispersity of the constituent particles [34]. With further increase in volume fraction above ϕ_{rcp} , the suspension exhibit domains of crystalline order. The particle volume fractions of these suspensions can be further increased up to the limit of hexagonal close packing, $\phi_{hcp} \approx 0.74$. It has been reported that the presence of size polydispersity in colloidal systems shifts the glass transition volume fraction to a slightly higher value [35–37]. In contrast, addition of charges on the particles shifts the glass transition volume fraction to lower values [38, 39]. For colloidal suspensions consisting of anisotropic particles, the glass transition volume fraction also depends on the shape of the particles [40–42]. Depending on the particle volume fraction, suspensions of regularly shaped anisotropic particles can also display other soft matter phases such as nematic or columnar phases [43, 44].

For suspensions of soft deformable colloidal particles, the glass transition volume fraction depends on the stiffness of the constituent particles [45, 46]. Due to their properties of compressibility and deformability, suspensions of soft colloidal particles exhibit the glass transition at particle volume fractions much above the random close packing volume fraction, ϕ_{rcp} , of monodisperse hard spheres. With varying volume fraction, suspensions of soft particles can exhibit other phases, such as a liquidcrystal coexistence phase [47]. When the volume fraction of uncharged or screened colloidal particles is below the glass transition volume fraction, a gel-like network can be formed due to interparticle attractive interactions such as hydrogen bonding, electrostatic attraction, and van der Waals attraction [48–50].

1.4 Colloidal systems approaching a jammed or kinetically arrested state

Suspensions of hard spheres are the most popular model systems used in the study of the jamming transition. When the concentration of colloidal particles in a sus-



Figure 1.3: (a) Jamming phase diagram proposed by Liu and Nagel [51] plotted in the planes of load σ , temperature T and the inverse of density $1/\phi$. This figure is adapted from [51]. (b) The jamming phase diagram for an attractive colloidal system proposed by Trappe *et al.* in the planes of $1/\phi$, k_BT/U and σ/σ_0 [52]. Here, U is the attractive potential between two colloidal particles of diameter a and $\sigma_0 = k_BT/a^3$.

pension increases, the suspension packing fraction increases, resulting in a jammed state. In the jammed, kinetically constrained or glassy state, each colloidal particle is confined/kinetically constrained by its neighbors in a phenomenon often known as caging [53] and the dynamics of the colloidal particles slow down by several orders of magnitude [29]. As a result, the characteristic structural relaxation time and the viscosity of the colloidal suspension increase drastically as the glass transition volume fraction is approached. This is reminiscent of the behavior of molecular glass formers, which display viscosities of the order of $\approx 10^{12}$ Pa.s near the glass transition temperature [54]. Colloidal glasses are fragile and can be unjammed by applying sufficient load. Based on these fundamental properties of the glass transition in complex systems, including granular matter, Liu and Negel have proposed a three dimensional jamming phase diagram as a function of load (σ), temperature (T) and inverse density ($1/\phi$). This phase diagram is reproduced in figure 1.3(a) [51]. According to this phase diagram, jamming or glass transition can be achieved by increasing the particle number density ϕ above a critical value. The kinetically arrested state of the system can be unjammed by applying load (stress, σ) or increasing system temperature, T. The boundaries between jammed and unjammed state is entirely system dependent. The jamming phase diagram therefore unifies the kinetic arrest phenomenon seen in different materials [51].

For attractive systems such as colloidal gels, the jamming phase diagram was later modified by Trappe *et al.* [52] (figure 1.3(b)). It is to be noted that, in contrast to the phase diagram of the repulsive hard sphere system (figure 1.3(a)), the phase diagram suggested by Trappe et al. [52] has opposite curvature due to the attractive nature of interparticle interactions. The phase diagram in figure 1.3(b), obtained via careful experiments, reveals that apart from applied stress σ (load) and particle density ϕ (concentration), the ratio of the thermal energy k_BT and the attractive interaction U between the particles also plays an important role in the kinetic arrest of the system. In the limit of low stresses, low attractive interactions and high particle concentration, the system exhibits glass-like amorphous behavior. In contrast, in the presence of strong attractive interactions at low stresses and high particle concentration, the system undergoes irreversible aggregation leading to the formation of clusters [55]. However, in the intermediate volume fraction limit, the system displays fractal network like structure [55]. The jamming phase diagrams discussed here can explain some common features of the jamming transition observed in most complex fluids. However, these phase diagrams fail to explain the shear induced jamming transition observed in some soft materials such as cornstarch suspensions [56] and the glass transition driven by physical aging in clay suspensions [57].

1.4.1 Growth of viscosity and relaxation times

It is well known that the viscosity of a liquid increases with decrease in temperature. If the liquid is cooled fast enough that the molecules do not get enough time to form an ordered structure, they enter into a mechanically strong disordered state. It has been reported that if the system's viscosity reaches a value of the order of $\approx 10^{12}$



Figure 1.4: Relative low shear viscosity η/η_0 vs. particle volume fraction ϕ for various colloidal suspensions constituted by nearly monodisperse hard spheres. Here, η_0 is the viscosity of the pure solvent. The solid line is the fit to equation 1.4. This figure is adapted from [2].

Pa.s [54], the system enters the glassy or a kinetically arrested state. In the case of a colloidal system, the viscosity of the suspension increases with volume fraction of the constituent particles. Figure 1.4 represents the plot of low shear relative viscosities, η/η_0 , for a colloidal suspension constituted by nearly hard spheres as a function of particle volume fraction ϕ [2, 58–60]. Here η and η_0 are the low shear viscosity of the suspension and viscosity of the solvent, respectively. From figure 1.4, we observe that the increase in viscosity to achieve the colloidal glass transition is of the order of $\approx 10^4$, much lesser than that required for the molecular glass transition.

In an important contribution, Marshall and Zukoski [61] performed experiments on colloidal suspensions constituted by silica hard spheres and showed that the viscosity of the suspension increases gradually with increase in particle volume fraction ϕ , followed by drastic increase in the viscosity above a certain value of ϕ . They reported that the viscosity vs. particle volume fraction data can be fitted to the Doolittle equation [62]:

$$\frac{\eta}{\eta_0} = C \exp\left[\frac{D\phi}{\phi_m - \phi}\right] \tag{1.4}$$

with C = 1.2, D = 1.65 and $\phi_m = 0.638$. Interestingly, the value of the fitting parameter $\phi_m = 0.638$ is very close to the random close packing fraction of monodisperse hard spheres, ϕ_{rcp} .

The colloidal glass transition can also be characterized by a drastic increase in the structural or α relaxation time scale and a simultaneous decrease in the diffusivity of constituent particles. For glassy systems, the self-diffusion coefficient D_L approaches zero. At the same time, time scales related to the microscopic structural relaxation process, τ_{α} increase rapidly as the glass transition is reached [2, 63]. τ_{α} and D_L are related to the radius of the colloidal particles, a, by the relation: $\tau_{\alpha} \propto a^2/D_L$. Therefore, the measurements of τ_{α} and D_L can explain the dynamical slowdown of a colloidal system near the glass transition. Interestingly, increase in τ_{α} with particle volume fraction also obeys the Doolittle equation and can be written as:

$$\tau_{\alpha} = \tau_0 \exp\left[\frac{D\phi}{\phi_m - \phi}\right] \tag{1.5}$$

where, D is a dimensionless parameter called fragility parameter or index.

In different glass formers such as molecular, colloidal and polymeric, the rates of growth of structural relaxations times and viscosity vary between different samples and the difference can be quantified in terms of the fragility index D [54]. As shown in figure 1.5, the viscosity or relaxation times of the fragile glass formers increase slowly up to some temperature or particle volume fraction value and grow drastically as the glass transition is achieved. On the other hand, strong glasses display Arrhenius behavior, where the logarithm of the viscosity or structural relaxation times increase linearly with the inverse of temperature, 1/T, as the glass transition is reached. The



Figure 1.5: Angell plots where logarithm of the viscosity of molecular liquids is plotted vs. inverse of the temperature normalized by the glass transition temperature T_g/T . Straight lines show the Arrhenius dependence of viscosity on temperature observed in strong glass formers (SiO₂, GeO₂ etc). Non-Arrhenius behavior of viscosity with temperature is observe for fragile glass formers (o-terphenyl, toluene etc.) and is represented by the deviation from the straight line. Inset shows the plot of the specific heat C_p as a function T/T_g . C_p which shows a jump at the glass transition temperature T_g . This figure is adapted from [54].

fragility index of molecular glass formers can be estimated by fitting the viscosity vs. temperature data to the Vogel-Fulcher-Tammann (VFT) equation [64–66]:

$$\frac{\eta}{\eta_0} = \exp\left[\frac{DT_0}{T - T_0}\right] \tag{1.6}$$

where, η_0 is the viscosity of the molecular liquid at a temperature $T \to \infty$ and T_0 is known as Vogel temperature, indicating the temperature at which the viscosity



Figure 1.6: (a) A single Laponite platelet (b) Schematic representation of the 2:1 crystalline structure of Laponite platelet. This figure is adapted from [70].

diverges [67]. The fragility, 1/D, of a glass former is defined as the deviation in the growth of viscosity from Arrhenius behavior upon quenching the system [54]. Increase in the value of 1/D indicates increase in the fragility of the glasses. In the case of colloidal glasses, where glass transition can be achieved by increasing the particle volume fraction, temperature T can be mapped with the inverse of volume fraction $1/\phi$ in equation 1.6. This results in a modified VFT equation:

$$\frac{\eta}{\eta_0} = \exp\left[\frac{D\phi}{\phi_0 - \phi}\right] \tag{1.7}$$

Using above equation, it has been reported that the values of D for colloidal glasses constituting hard spheres lie between 1-2 [58, 61]. This equation can also be used for structural relaxation times just by mapping η/η_0 with τ_{α}/τ_0 [68, 69]. The fragility of colloidal glass formers depends on various parameters such as size polydispersity, stiffnesses of the constituent particles and interaction potential between the particles [8, 37, 45, 46].

1.5 Aging and phase behavior of synthetic clay colloids

Hydrous sodium lithium magnesium silicate $(Na_{+0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7})$ or Laponite[®] is a 2:1 synthetic clay having structure resembling that of natural hectorite clay minerals belonging to the smectite family. As shown in figure 1.6(a), Laponite particles are disc-shaped and each particle has a lateral dimension of ≈ 25 nm and a thickness of ≈ 1 nm [71–74]. With an octahedral configuration of magnesium in between two tetrahedral silica sheets (figure 1.6(b)), this clay mineral acquires a net negative charge on its surfaces due to the isomorphic substitution of divalent Mg with monovalent Li atoms [75]. In dry form, Laponite exists as stacks of tactoids with Na⁺ ions in the inter-layer gallery that compensate the negative charges on the particle surfaces. The edge charges are pH dependent such that when Laponite particles are dispersed in an aqueous medium, their edges become more positively charged with decrease in pH [76–79]. When Laponite is dispersed in water, the water molecules diffuse into the intra-gallery spaces of the clay platelets and hydrate the sodium counterions, thereby causing the tactoids to swell and eventually exfoliate [80]. Due to the gradual buildup of osmotic pressure gradients in the sample, the sodium ions diffuse into the bulk, creating excess negative charges on the Laponite surfaces [24, 81]. This is accompanied by the formation of an electrical double layer (EDL) that evolves with time due to the time-dependent development of interparticle interactions. The positively charged EDLs repel strongly, leading to physical aging and eventual kinetic arrest of the Laponite platelets at long waiting times, t_w . The aging dynamics and self-assembled structures formed in Laponite suspensions are, therefore, attributed to the growth of time-dependent interparticle electrostatic interactions that depend on the particle and ionic concentrations [9, 57, 81–87]. The physicochemical properties of Laponite suspensions can be effectively tuned by controlling the interparticle interactions via external additives, applied electric field and by varying the dispersion temperature [24, 88, 89].



Figure 1.7: Phase diagram of Laponite suspensions proposed by Ruzicka *et al.* [9]. VI, LS, SIM, SAXS, DLS and SLS are refer to visual inspection, light scattering, numerical simulations, small angle X-ray scattering, dynamic light scattering and static light scattering respectively. This figure is adapted from [9]. The details of the references mentioned in the figure can be found in [9].

For suspensions of Laponite above 2wt%, the viscosity and elastic modulus increase gradually over time. This suggests a continuous structure build-up in a process commonly known as physical aging [90–92]. In dynamic light scattering experiments, the aging behavior of these suspensions is manifested by an enhancement in the structural relaxation time with increase in waiting time [57, 93]. However, the application of shear stresses reverses the process of aging, with the viscosity, elastic modulus and relaxation time of the suspension decreasing due to the breakdown of the sample microstructure [91, 94]. This process is known as rejuvenation for colloidal glasses and shear melting in the rheology literature [95].

The phase diagram of aqueous Laponite suspensions has been extensively debated in the literature and the understanding has evolved considerably over time [9, 84, 87]. A state diagram of Laponite suspensions proposed by Ruzicka *et al.* [9] indicates that the suspensions undergo phase separation below 1% w/w and forms an attractive gel between 1 to 2% by forming links between negatively charged surfaces and positively charged rims [86, 96] (figure 1.7). Above 2% w/w, a repulsive Wigner glass is reported wherein each particle is trapped in a cage formed by surrounding particles [97]. A recent study claimed that the system exists in an attractive gel state even at higher particle concentrations [98]. Laponite suspensions can also show fascinating phase behavior with varying salt concentration [99, 100]. A gel or a glass state and a nematic gel state have been reported at low salt concentrations with increase in clay concentration. At very high ionic strengths, phase separation has been reported [101]. Several studies have shown that the phases and aging kinetics of Laponite suspensions are sensitive to sample preparation protocols. In dynamic light scattering studies, filtering the sample immediately after preparation delays aging kinetics, indicating a reduction in the number density of clusters present in the sample [102, 103]. However, Bonn *et al.* have reported that the bulk rheological behavior of Laponite clay colloidal suspensions is insensitive to the filtration process [102].

1.6 Thermoresponsive microgels

Microgels are three dimensional crosslinked networks of hydrophilic polymers which can absorb and retain a large amount of water. Based on the chemical and physical nature of the crosslinking junctions, microgels can be divided into two categories. Chemically crosslinked networks are irreversible in nature and can be formed by the polymerization process. In contrast, physically crosslinked networks have transient junctions, which can arise from either polymer chain entanglement or physical interactions such as hydrogen bonding or hydrophobic and ionic interactions. Due to their tunable properties as well as their versatile fabrication methods, microgels have been used in biomedical and engineering applications, tissue engineering and



Figure 1.8: Schematic illustration of a thermoresponsive PNIPAM microgel particle. This figure is adapted from [104]. PNIPAM chains are crosslinked to form a spherical particle. At low temperatures, the particle size is larger due to absorption of water by the particle. When the temperature is increased, the particle expels water and shrinks to a smaller size.

regenerative medicine, for wastewater treatment and soft robotics.

1.6.1 Thermoresponsive poly(*N*-isopropylacrylamide) (PNI-PAM) microgel particles

Thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) microgel particles are spherical shaped particles consisting of crosslinked PNIPAM chains and water (figure 1.8). When dispersed in water, these particles show swelling and deswelling behaviors respectively below and above the lower critical solution temperature (LCST, also referred to as the volume phase transition temperature, VPTT) of $\approx 34^{\circ}$ C [105, 106]. Below the LCST, the hydrophilic amide groups of PNIPAM form hydrogen bonds with water molecules such that individual PNIPAM particles absorb water and swell significantly. Due to increased entropy above the LCST, water molecules reorient around the non-polar regions of the PNIPAM macromolecules, thereby restricting hydrogen bond formation with the constituent amide groups. PNIPAM particles, therefore, exhibit hydrophobic behavior above their LCST and shrink by expelling



Figure 1.9: (a) Scanning electron micrograph of PNIPAM particles in dry state. (b) Average hydrodynamic diameter $\langle d_H \rangle$ of the PNIPAM particles in aqueous suspension is plotted as a function of temperature while heating and cooling.

water [107]. As a consequence of this thermoreversible swelling behavior, the volume fraction of PNIPAM particles in aqueous suspensions can be controlled simply by altering the temperature of the medium at a fixed particle concentration [108]. This offers an advantage over many temperature-insensitive hard colloidal particles such as poly(methyl methacrylate) (PMMA) and polystyrene (PS). Dense aqueous suspensions of PNIPAM particles have therefore been recognized as excellent model colloidal systems in the study of glass transition dynamics [37, 104]. Various protocols, for example, synthesizing the particles in different ionic liquids or changing the concentration and nature of crosslinkers during synthesis have been implemented to alter the LCST of these particles [109]. Besides being thermoresponsive, PNIPAM particles are deformable and compressible in aqueous suspensions at high particle volume fractions and a fixed temperature. Given their compressibility and deformability, these particles can be packed well above the random close packing fraction of monodisperse hard spheres, $\phi_{rcp} = 0.64$. The unique characteristics of PNIPAM particles have led to their use as drug delivery agents [110, 111] and biosensors [112].

PNIPAM microgel particles can be synthesized using free radical precipitation polymerization or one-pot and semi-batch methods [37, 113]. PNIPAM particles of

different sizes and stiffnesses can be synthesized by changing the concentration of surfactant and crosslinker during the synthesis process [114–116]. These particles in their dry state can be clearly seen under a scanning electron microscope (SEM). Figure 1.9(a) shows an SEM image of PNIPAM microgel particles in a dry state at room temperature. The thermoresponsive behavior of aqueous suspensions of PNI-PAM particles can be studied using the dynamic light scattering (DLS) technique. Figure 1.9(b) represents the plot of average hydrodynamic diameter, estimated using DLS measurements, as a function of temperature for dilute aqueous suspensions of PNIPAM particles. It is noted that the sizes of these particles decrease very rapidly with increase in temperature at the LCST, while the two plateaus observed at lower and higher temperatures indicate fully swollen and shrunken state of PNI-PAM particles, respectively. It is clear from figure 1.9(b) that PNIPAM particles are thermoreversible in aqueous suspensions since the particle diameters remain the same regardless of whether the measurement is performed during the heating or the cooling cycles.

1.6.2 Thermoresponsive core-shell particles

Thermoresponsive core-shell particles used in this thesis are synthesized using a combination of two thermoresponsive polymers. Core-shell particles, with the shell composed of poly(*N*-n-propylacrylamide) (PNNPAM) with LCST of $\approx 21^{\circ}$ C and the core made of poly(n-iso-propylmethacrylamide) (PNIPMAM) polymers with LCST $\approx 44^{\circ}$ C, are synthesized using two-step free radical precipitation polymerization method [117, 118]. The combination of different monomers forming the particle's core and shell produces a microgel with extraordinary linear swelling properties [117]. The linear swelling property is achieved because of the large gap of $\approx 23^{\circ}$ C between the LCTSs of the core and shell-forming polymers. Figure 1.10 shows an SEM image of the thermoresponsive core-shell particles at room temperature in a dry state. The core and shell are distinguishable in the SEM image.



Figure 1.10: Scanning electron micrograph of thermoresponsive core-shell particles in dry state.

1.7 Thesis organization

This thesis systematically investigates the jamming dynamics and rheological and phase behaviors of colloidal suspensions formed by Laponite clay and thermoresponsive microgel particles. Chapter 1 briefly describes interparticle interactions in colloidal suspensions and glass transitions in colloidal and molecular systems. It also discusses the aging dynamics and phase behavior of Laponite clay and the thermoresponsive nature of microgel particles. Various experimental techniques and synthesis protocols are described in chapter 2. The effects of medium structure (which is water in the present case) on the physicochemical properties of aging colloidal suspensions of the synthetic clay Laponite are discussed in chapter 3. Chapter 4 describes the effect of temperature and two different sample preparation protocols on the aging dynamics of aqueous Laponite suspensions. The effect of changing surfactant concentration during the synthesis procedure on the thermoresponsive and rheological behaviors of PNIPAM particles are discussed in detail in chapter 5. The rheological behavior and particle self-assembly of dense PNIPAM suspensions constituting particles of different stiffnesses and at different suspension temperatures are described in chapter 6. Chapter 7 reports the use of the rheo-dielectric technique in studying the dynamical behavior of dense suspensions of soft glassy materials at different length scales. Chapter 8 reports a linear and non-linear rheological study of dense suspensions of thermoresponsive core-shell microgel particles. Effects of varying the stiffness of the core particles on the thermoresponsive and rheological properties of aqueous suspensions of thermoresponsive core-shell particles are discussed in chapter 9. Chapter 10 contains a summary of the experimental results reported in this thesis and discusses the scope of future research.

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Chapter 2

Materials, Synthesis Methods and Experimental Techniques

2.1 Introduction

This chapter discusses sample preparation, synthesis methods and experimental techniques that are used in this thesis to study aqueous colloidal suspensions. Thermoresponsive colloidal particles of different sizes and stiffnesses are synthesized using free radical precipitation polymerization or one-pot synthesis methods. Dynamic light scattering is used to study the microscopic dynamics of aging colloidal suspensions and the thermosensivity of thermoresponsive colloidal particles. The bulk rheological properties of the aqueous colloidal suspensions are studied using a commercially available rheometer. A rheometer is interfaced with a precision impedance analyzer to study the rheo-dielectric properties of the samples. Scanning electron microscopy (SEM) is used to directly visualize colloidal particles in a dried state and characterize the particle size and size distribution. Cryogenic electron microscopy (cryo-SEM) is used to investigate the morphologies of colloidal suspensions. Differential scanning calorimetry (DSC) is used to study the lower critical solution temperature of aqueous suspensions of thermoresponsive colloidal particles.

2.2 Synthesis methods and sample preparation

2.2.1 Preparation of aqueous Laponite[®] suspensions

All the experiments on physical aging of colloidal suspensions are performed with Laponite XLG[®]powder (purchased from BYK Additives Inc., molecular weight-2286.9 g/mol). Before each experiment, Laponite powder is dried in an oven at 120°C for 18 hours to remove moisture. The dried powder is weighed and added to Milli-Q water (Millipore Corp., resistivity 18.2 MΩ-cm) which is continually agitated using a magnetic stirrer for 45 minutes. For the dynamic light scattering experiments, a freshly prepared sample is filtered through a Millipore filter of diameter 33 mm and pore size 0.45 μ m into the glass cuvette using a syringe. The increase in the sample waiting time, t_w , is monitored continuously from the time at which filtration was stopped ($t_w = 0$ at the completion of the filtration procedure). For the rheological measurements, the suspensions are loaded immediately after preparation. The sample is rejuvenated/shear melted by applying a high shear rate of 1500 s⁻¹ for 3 minutes. This is done to remove the residual stresses due to the loading of the sample in the rheometer geometry and to achieve a reproducible starting point for all experiments.

2.2.2 Synthesis of thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) particles

PNIPAM particles are synthesized using free radical precipitation or the one-pot polymerization method [1]. Thermoresponsive polymers phase separate from a homogeneous binary mixture of solvent and polymer when the temperature of the medium increases above a critical value [2]. The transition temperature is known as lower critical solution temperature (LCST) and originates from the temperature dependent interaction energies of the components of the binary polymer-solvent system [1]. Free radical precipitation polymerization of monomers produces thermosensitive polymers above the phase separation temperature of the polymer [3]. In such a free radical polymerization process [3], the monomer and initiator are soluble in the continuous phase, but the product phase separates or precipitates during the reaction. Well stabilized spherical polymer particles of narrow size distribution in the size range of tens of nanometers upto a few micrometers can be synthesized using free radical precipitation polymerization reaction [3].

All the chemicals are purchased from Sigma-Aldrich and are used as received without any further purification. In the typical polymerization reaction, a predetermined amount of N-isopropylacrylamide (NIPAM) monomer ($\geq 99\%$), crosslinker N, N'-methylenebisacrylamide (MBA) ($\geq 99.5\%$) and sodium dodecyl sulfate (SDS) are dissolved in Milli-Q water (Millipore Corp.) in a three-necked round-bottom (RB) flask attached with a reflux condenser, a magnetic stirrer with heating (Heidolph), a platinum sensor and a nitrogen gas (N_2) inlet/outlet. The solution is then stirred at 600 RPM and purged with N_2 gas for 30 minutes to remove the oxygen present in the solution. Dissolution of potassium persulphate (KPS) (99.9%) in Milli-Q water after heating the mixture to 70°C initiated the reaction. The reaction is allowed to proceed for 4 hours with a constant stirring speed of 600 RPM and the suspension is then cooled down to room temperature. The suspension is next purified by four successive centrifugations and re-dispersions at a rotational speed of 15,000-50,000 RPM for 60 minutes to remove SDS, the remaining monomers, oligomers, and impurities. After the centrifugation, the supernatant is removed and the remaining sample is dried by evaporating the water. A fine powder is prepared by grinding the dried particles using a mortar and pestle.

In this thesis work, concentrations of surfactant (SDS) and crosslinker (MBA) are varied to synthesize PNIPAM particles of different sizes and stiffnesses.

2.2.3 Synthesis of thermoresponsive core-shell particles

Thermoresponsive core-shell particles with shells composed of poly(*N*-n-propylacrylamide) (PNNPAM) with LCST of $\approx 21^{\circ}$ C and cores consisting of poly(n-iso-propylmethacrylamide) (PNIPMAM) of LCST $\approx 44^{\circ}$ C are synthesized using a two-step free radical precipitation polymerization method [4, 5]. The combination of distinct monomers forming the particle's core and shell produces a hydrogel with extraordinary linear swelling properties. The linear swelling property is achieved because of the large gap of $\approx 23^{\circ}$ C between the LCTSs of the core and shell-forming polymers.

2.2.3(a). Synthesis of shell monomer

N-n-propylacrylamide (NNPAM) monomer is synthesized following the Schotten-Baumann reaction described elsewhere [6]. The Schotten-Baumann reaction can be used to synthesize amides from amines and acid chloride. In the synthesis process, a solution of n-propylamine (24.62 mL) and triethylamine (41.25 mL) is first prepared in 100 mL dichloromethane and stirred at 400 RPM (solution 1). Solution of acryloyl chloride (20.22 mL) is next prepared in 50 mL dichloromethane (solution 2). Solution 2 is added to solution 1 dropwise at temperature 3-5°C under stirring condition. The mixture is stirred for 24 hours at room temperature. After 24 hours the mixture is washed with solution of 10% of sodium bicarbonate (NaHCO₃) in Milli-Q water and dried using magnesium sulfate (MgSO₄). The remaining solution is then filtered and dichloromethane (reaction medium) is evaporated using a rotavapor. Distillation in vacuum (91-95°C, 3 mm Hg) produces pure NNPAM monomer.

2.2.3(b). Synthesis of core poly(n-iso-propylmethacrylamide) (PNIP-MAM) particles

PNIPMAM particles are synthesized using the free radical precipitation polymerization process [4, 5]. All the chemicals are purchased from Sigma-Aldrich and are used as received without any further purification. In the typical polymerization reaction, predetermined amounts of n-iso-propylmethacrylamide (NIPMAM) monomer ($\geq 99\%$), crosslinker N, N'-methylenebisacrylamide (MBA) ($\geq 99.5\%$) and sodium dodecyl sulfate (SDS) are dissolved in 370 mL Milli-Q water (Millipore Corp.) in a three-necked round-bottom (RB) flask attached with a reflux condenser, a magnetic stirrer with heating (Heidolph), a platinum sensor and a nitrogen gas (N₂) inlet/outlet. The solution is then stirred at 400 RPM and purged with N₂ gas for 30 minutes to remove the oxygen present in the solution. Dissolution of ammonium persulphate (APS) (99.9%) in Milli-Q water after heating the mixture to 70°C initiated the reaction. The reaction is allowed to proceed for 4 hours at the constant stirring speed of 400 RPM. The suspension is then cooled down to room temperature and purified by four successive centrifugations and re-dispersions at a rotational speed of 15,000-45,000 RPM for 60 minutes to remove SDS, the remaining monomers, oligomers, and impurities. After the centrifugation, the supernatant is removed and the remaining sample is dried by evaporating the water. A fine powder is prepared by grinding the dried particles using a mortar and pestle.

2.2.3(c). Synthesis of thermoresponsive core-shell particles

To synthesize thermoresponsive core-shell particles, 0.6 g of core (PNIPMAM) particles are well dispersed in 200 mL of Milli-Q water. The core particles dispersed in water are then coated with 2.08 mL of shell monomer and 0.048 g of MBA (2.5% of the shell monomer) using 0.128 g SDS and 0.248 g APS following the free radical precipitation method as described above. After synthesis, the same purification steps are followed as discussed before to get the powder of pure thermoresponsive core-shell particles.

Experimental techniques

2.3 Dynamic light scattering

Dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS), is a potent tool for studying the microscopic motion of macromolecules in suspensions. DLS is widely used to determine the particle size, size distribution profile, structure and dynamics of colloidal particles in suspensions.

A monochromatic and coherent source or laser, an index-matching bath with a sample holder, a high-speed and efficient detector (photomultiplier tube (PMT) or avalanche photodiode (APD)) and an auto-correlator are the main components of a dynamic light scattering (DLS) setup. A schematic diagram and a picture of our DLS setup are shown in figure 2.1. In dilute suspensions, colloidal particles exhibit Brownian motion due to constant collisions with the molecules of the medium. Particles with sizes that are smaller than the wavelength of the incident light will scatter the incident light in all directions via the Rayleigh scattering process. The intensity of the scattered light has an angular dependence and fluctuates due to Brownian motion of the suspended particles. The intersection of the incident laser beam and the beam intercepted by the detector is defined as the scattered light is used to measure the shape and size (hydrodynamic diameter) of colloidal particles in dilute suspensions. Below is a brief description of the theory for measuring the sizes of monodisperse spherical colloidal particles diffusing in a dilute suspension.

If the scattering volume V containing N identical scatterers is illuminated with a monochromatic plane wave of frequency ω_0 polarized perpendicular to the scattering plane, then the light scattered by the *j*th scatterer at a distant point R_0 and at a scattering angle θ is given by [8, 9]:



Figure 2.1: (a) A schematic diagram of a dynamic light scattering (DLS) setup. (b) Photograph of BIC 200SM DLS setup with a laser (A), a index matching bath (B) a sample holder (C) and a photo multiplier tube (D).

$$E_j = A_j(t) \exp(i\phi) \exp(-i\omega_0 t)$$
(2.1)

where A_j is the amplitude of the field E_j . If we consider phase $\phi = 0$ for the scatterer situated at the origin then according to figure 2.2, the phase for the *j*th scatterer with a position vector r_j with respect to the origin will be [8]

$$\phi_j = (\vec{K_0} - \vec{K_s}) \cdot \vec{r_j} = \vec{q} \cdot \vec{r_j}$$
(2.2)



Figure 2.2: Schematic diagram of the geometry of a scattering system.

In equation 2.2, $\vec{K_0}$ and $\vec{K_s}$ are the incident and scattered wave vectors respectively. For quasi-elastic light scattering, $|\vec{K_0}| \approx |\vec{K_s}|$ and $|\vec{q}| = 2|\vec{K_0}|\sin(\theta/2) = \frac{4\pi n}{\lambda}\sin(\theta/2)$, where n and λ are the refractive index of the medium and wavelength of the incident light respectively [7, 10]. The total scattered field, E_s , at a distance R_0 will be [8]:

$$E_{s} = \sum_{j=1}^{N} A_{j}(t) e^{i\vec{q}\cdot\vec{r_{j}}} e^{-i\omega_{0}t}$$
(2.3)

The total average scattered intensity at distance R_0 is given by:

$$I_s = \left\langle |E_s|^2 \right\rangle \tag{2.4}$$

where the angular bracket $\langle \rangle$ denotes an average over time. Since the motion of the scatterers are uncorrelated and independent, all cross terms in the expression of I_s vanish to give [8]:

$$I_s = \left\langle \sum_{j=1} |A_j|^2 \right\rangle = N \left\langle |A|^2 \right\rangle \tag{2.5}$$

The expression for the spectrum of the scattered light can be obtained using Wiener-

Khintchine theorem [11]:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(\tau) e^{i\omega\tau} d\tau$$
(2.6)

where $C(\tau)$ is the electric field autocorrelation and given by:

$$C(\tau) = \left\langle E_s^*(t)E_s(t+\tau) \right\rangle \tag{2.7}$$

Here, E_s^* is the complex conjugate of E_s . Substituting the values of E_s and E_s^* in the expression for $C(\tau)$ and assuming that the positions and orientations of all the scatterers are independent, we get:

$$C(\tau) = N e^{-i\omega_0 \tau} \langle A^*(t) A(t+\tau) \rangle \left\langle e^{-i\vec{q}\cdot\vec{r}(t)} e^{i\vec{q}\cdot\vec{r}(t+\tau)} \right\rangle$$
(2.8)

where all the N scatterers are identical and have the same autocorrelation function. Substituting the value of $C(\tau)$ in equation 2.6, for identical and statistically independent scatterers we get,

$$I(\omega) = \frac{N}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega - \omega_0)\tau} [C_A(\tau)] [C_\phi(\tau)] d\tau$$
(2.9)

where $C_A(\tau)$ and $C_{\phi}(\tau)$ are the amplitude autocorrelation functions and phase autocorrelation functions respectively. The scattering amplitude A(t) is constant for identical spherical scatterers undergoing translational diffusion. Therefore, $[C_A(\tau)] = 1$ and the phase autocorrelation function is given by $[C_{\phi}(\tau)] = e^{-Dq^2\tau}$ [8], where D is the translational diffusion coefficient and is related to the hydrodynamic radius r_h of the scatterer by the Stokes-Einstein relation [12],

$$D = \frac{k_B T}{6\pi\eta r_h} \tag{2.10}$$

where k_B is the Boltzmann constant, η is the viscosity of the suspension medium at temperature T.

Depending on the optical mixing methods of the scattered spectrum, there are two types of DLS measurements: homodyne and heterodyne. In the homodyne measurement, the scattered spectrum is mixed with itself. In heterodyne measurements, however, a part of the incident beam is mixed with the scattered beam. Homodyne measurements are employed for all the DLS measurements reported in this thesis. In this method, the output of the detector is either analyzed by an autocorrelator to generate the autocorrelation function or is sent to a spectrum analyzer. The instantaneous intensity I(t) of the spatially coherent optical field is related to the electric field E(t) by the relation: $I(t) = E^*(t)E(t)$. The second-order intensity autocorrelation function $g^{(2)}(\tau)$ can therefore be related to the first-order electric field autocorrelation function $g^{(1)}(\tau)$ by the Siegert relation [13]:

$$g^{(2)}(\tau) = 1 + A|g^{(1)}(\tau)|^2$$
(2.11)

Where $g^{(1)}(\tau) = \langle E^*(t)E(t+\tau)\rangle / \langle E^*(t)E(t)\rangle$, $g^{(2)}(\tau) = \langle E^*(t)E(t)E^*(t+\tau)E(t+\tau)\rangle / \langle E^*(t)E(t)\rangle^2$ and A is the coherence factor. For a dilute suspension of identical spherical scatterers undergoing translational diffusion, $g^{(1)}(\tau) \propto e^{-Dq^2\tau}$ [8] and therefore $g^{(2)}(\tau) - 1 \propto e^{-2Dq^2\tau}$.

DLS experiments reported in this thesis are performed using a Brookhaven Instruments Corporation (BIC) BI-200SM spectrometer attached with a 150 mW solid state laser (NdYVO₄, Coherent Inc., Spectra Physics Excelsior) having an emission wavelength of 532 nm (figure 2.1(b)). A glass cuvette filled with the suspension is held in a refractive index matching bath filled with decaline. The temperature of the sample cell is controlled with a temperature controller equipped with a water circulation unit (Polyscience Digital). The photons scattered from the sample produce secondary electrons inside the detector, which sets off voltage pulses in the PMT [14]. The autocorrelation function of light scattered from the sample is measured using a Brookhaven BI-9000AT digital autocorrelator connected to the output of the detector at scattering angles between 45° to 135° . The BI-9000AT is a high-speed signal processor that operates in real-time over 10 decades of delay times. The scattered photon pulses are registered in autocorrelator channels, which can be segregated by logarithmically or linearly spaced delay times. The maximum number of channels that are used in the autocorrelator is 522 (26 channels for high-speed circuits, 256 channels for medium speed and 240 channels for low speed) [14]. The intensity autocorrelation function $g^{(2)}(\tau)$ is estimated by the autocorrelator using the following expression:

$$g^{(2)}(\tau_j) = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{\infty} n_i n_{i-j} \qquad j = 1, 2, \dots, M$$
(2.12)

where τ_j is the *j*th delay time, *N* is the total number of samples, n_i and n_j are the number of pulses in the sampling time $\Delta \tau$ centered at *t* and $t - \tau_j$ respectively and *M* is the total number of correlator channels [14]. The average number of pulses $\langle n \rangle$ in a time interval $\Delta \tau$ can be estimated from the average count rate $\langle CR \rangle$ using the relation $\langle n \rangle = \langle CR \rangle \Delta \tau$ [14].

2.3.1 Data analysis

Figure 2.3(a) shows the normalized intensity autocorrelation function, $C(\tau) = g^{(2)} - 1$, as a function of delay time, τ , for a dilute suspension of polystyrene (PS) particles (volume fraction $\phi = 10^{-5}$ prepared from the stock suspension) at different scattering angles θ and at a temperature $T = 25^{\circ}$ C. The average size of the PS particles is 152 nm with a polydispersity of 3.7% as given by the manufacturer (Bangs Laboratories Inc.). The second order intensity autocorrelation function at a scattering angle θ is given by $g^{(2)}(\tau) = \frac{\langle I(0)I(\tau) \rangle}{\langle I(0) \rangle^2} = 1 + A|g^{(1)}(\tau)|^2$ [7], where $I(\tau)$, $g^{(1)}(\tau)$ and A are the intensity at a delay time τ , the normalized electric field autocorrelation function and the coherence factor, respectively and the angular bracket $\langle \rangle$ is an average over time. The normalized intensity autocorrelation functions, obtained at seven different scattering angles which correspond to seven different wave vectors q, are fitted to exponential functions of the form $C(\tau) = [\exp(-\tau/\tau_1)]^2$, where τ_1 is the re-



Figure 2.3: (a) Normalized intensity correlation function $C(\tau)$ vs. delay time τ for scattering from 152 nm polystyrene (PS) particles in a dilute aqueous suspension at temperature 25°C and at different scattering angles θ . The solid lines are fits to the equation: $C(\tau) = [\exp(-\tau/\tau_1)]^2$. (b) $1/\tau_1$ vs. q^2 plot showing diffusive nature of PS particles. The diffusion coefficient D, extracted from the slope of the linear fit (solid line), yields 153 ± 1 nm as the size of the PS particle.

laxation time of the PS particles. Figure 2.3(b) represents the plot of $1/\tau_1$, obtained from the fits to the $C(\tau)$ vs. τ data, as a function of q^2 . A straight line passing through the origin (solid line in figure 2.3(b)) demonstrates the diffusive behavior of the relaxation process *i.e.* $1/\tau_1 = Dq^2$. Here, D is the diffusion coefficient and is estimated from the slope of the $1/\tau_1$ vs. q^2 plot. The size of the polystyrene particles suspended in aqueous medium ($\eta = 0.89$ mPa.s at 25°C) is calculated using the Stokes-Einstein relation (equation 2.10). The estimated size of the PS particle used here is 153 ± 1 nm, which matches closely with the size given by the manufacturer.

2.4 Rheological measurements

Rheology deals with the study of flow and deformation of materials under applied stresses or strains [15]. The term rheology was coined by Professor E. C. Bingham at Lafayette College in Indiana and its goal is to establish relationships between forces (stresses) and deformations (strains) in viscoelastic materials where Newton's law [16] and Hooke's law [17] alone would fail to explain their mechanical behav-



Figure 2.4: (a) The Anton Paar MCR 702 rheometer. (b) Schematic diagram of the main components of Anton Paar MCR series rheometers fitted with a cone-plate measuring geometry.

ior [15]. Rheology is relevant in many fields including industrial and technological applications such as concrete technology, polymers, geology, plastics processing composites, paint flow, etc.

In the laboratory, the flow behavior of materials can be studied by estimating various rheological parameters using a rheometer. Depending on the control parameters (stress and strain), a rheometer can be used either in stress or strain-controlled modes. A rheometer with strain control measures stresses by applying a shear strain (constant or time-dependent). On the other hand, stress-controlled rheometers apply shear stresses (constant or time dependent) to the material and measure the resulting strain. The rheological experiments reported in this thesis are performed

using stress-controlled modular compact Anton Paar MCR 501 and MCR 702 (figure 2.4(a)) rheometers. These rheometers can also be used to control strain or shear rate through a feedback mechanism [18]. Figure 2.4(b) shows the schematic illustration of a rheometer. There are three key components of the MCR series rheometers: optical encoder, synchronous motor and air bearing. The high resolution optical encoder measures the deformation (strain) that is applied using the software and enables precise measurement and control of angular deflections with a resolution < 1 μ rad.

The air bearing supported synchronous electrically commutated (EC) DC motor consists of permanent magnets. A small rotor disc mounts these magnets and produces a constant magnetic field, providing a delay-free response. The rotor moves synchronously with the stator field produced by a series of coils. Dust and moisturefree compressed air from the compressor is supplied to the air bearing, allowing the motor's friction-free motion. With the help of this technology, one can achieve shallow torque measurements down to a minimum of 0.5 nN.m with a resolution of 0.01 nN.m [18]. The normal force transducer attached to the air bearing measures the normal forces during both transient and steady state measurements. It also detects the natural movement of the air bearing and converts the small deflections into normal forces in the range between 0.01 µN.m to 300 mN.m with a resolution of 0.01 nN.m [18]. The rheological data presented in this thesis are acquired using the RheoCompass software in MCR 702 and the Rheoplus software in MCR 501 rheometers. The temperature of the sample under study is controlled using Peltier (temperature range between 0° C and 180° C) and water circulation (Viscotherm VT2) (temperature range between 5°C and 80°C) devices.

For different rheological measurements, a measuring geometry is connected to the rotating rod of the rheometer and is automatically detected. The desired gap size for measurements using this geometry is achieved using TruGapTM [18] technique which eliminates errors arising from thermal expansion and non-zero normal forces.



Figure 2.5: Schematic diagram of different rheometer geometries: (a) concentric cylinder geometry and (b) double gap geometry, (c) cone-plate geometry and (d) parallel plate geometry. The figure is adapted from [18].

Depending on the property of the system under study and our experimental requirements, different measuring geometries can be used. These geometries are discussed below:

2.4a. Concentric cylinder geometry

As shown in figure 2.5(a), a concentric cylinder geometry (CC-17) comprises a coaxially arranged cylindrical cup and a rotating cylindrical bob. The concentric cylindrical geometry is useful for low-viscosity liquids. The CC-17 geometry has a gap of 0.71 mm and an effective length of 24.99 mm. A sample volume of 4.72 mL is kept in the annulus between the cylindrical surfaces for the measurements.

2.4b. Double gap geometry

The double gap geometry is a specially designed concentric cylinder geometry consisting of a rotating hollow inner cylinder placed in a cylindrical groove of the outer cylinder (figure 2.5(b)). The sample is filled in the double annular gap, providing a larger contact area that increases the measurement accuracy for very low viscosity fluids. The double gap DG-26.7 geometry, used for our rheological measurements, has an internal measuring gap of 0.41 mm, an external measuring gap of 0.46 mm, an effective length of 40 mm and requires a sample volume of 3.8 mL for each run.



Figure 2.6: (a) Viscosity (blue) and shear stress (red) as a function of shear rate for silicone oil at 25° C. (b) Viscosity (blue) and shear stress (red) vs. shear rate for a 10wt.% aqueous poly(N-iso-propylacrylamide) (PNIPAM) suspension at 25° C.

2.4c. Cone and plate geometry

In a cone and plate geometry, the sample is placed in between a rotating inverted cone and a fixed flat plate (figure 2.5(c)). The cone and plate geometry is useful for rheological measurements of high viscosity samples such as gels, pastes and concentrated colloidal suspensions. In the cone-plate geometry, the upper cone shape maintains a constant shear rate within the entire gap. The cone-plate CP-25 geometry, used for our rheological experiments, has a measuring gap d = 0.048 mm with cone radius $r_c = 12.49$ mm and cone angle $\alpha = 0.979^{\circ}$. The truncation of the cone in this geometry is $48 \ \mu$ m. In CP-25 geometry, a very small sample volume of 0.07 mL is required for each experiment.

2.4d. Parallel plate or plate-plate geometry

In a parallel plate geometry, also called plate-plate geometry, both upper (rotating) and lower (stationary) plates are flat (figure 2.5(d)) and the gap between the two plates can be controlled. The parallel plate geometry used by us, PP-25, has an upper plate diameter of 25 mm and requires a sample volume of 1.96 mL at a gap of 1 mm in each run. Unlike cone-plate geometry, parallel-plate geometry does not provide constant shear rates throughout the gap.

2.4.1 Applications of the rheometer

Using a rheometer, several distinct and useful rheological measurements can be performed to study the sample under flow. A rheometer has two basic modes of operation, viz. rotational and oscillatory.

2.4.1a. Rotational rheology

In rotational rheology, the flow properties of a sample are measured by applying a rotational shear rate or strain and by recording the resulting shear stress response or viscosity. The flow properties of soft materials that are often investigated using rotational rheology are shear thickening, shear thinning, shear banding, creep and stress relaxation behaviors. Flow curves and viscosity measurements are the rotational experiments that we performed for this thesis work to measure the shear stresses and viscosities of the samples. The flow curve is measured by varying shear rate $\dot{\gamma}$ or stress σ and measuring the response in terms of σ or $\dot{\gamma}$ respectively. The flow curve and the corresponding viscosity plot ($\eta vs. \dot{\gamma}$) of silicone oil is shown in figure 2.6(a). It is seen that the viscosity η of silicone oil is independent of applied shear rate $\dot{\gamma}$, thereby revealing its Newtonian liquid behavior. Figure 2.6(b) shows the flow curve of a 10wt.% aqueous poly(*N*-iso-propylacrylamide) (PNIPAM) suspension at 25°C. The viscosity of PNIPMAM suspension decreases with increasing shear rate, reflecting the shear thinning viscoelastic behavior of the sample.

2.4.1a(i). Effective volume fraction estimation of soft and deformable colloidal particles using rotational rheology

Soft colloidal particles such as PNIPAM can deform when packed above the random close packing volume fraction of undeformed monodisperse spheres ($\phi_{rcp} = 0.64$). Since the volume fraction ϕ is not appropriate for quantifying the packing of soft deformable particles in suspension, a modified parameter called the effective volume fraction, ϕ_{eff} , has been used. The effective volume fractions, ϕ_{eff} , of the aqueous



Figure 2.7: Relative viscosity η_{rel} vs. concentration c of PNIPAM particles in aqueous suspensions. The solid line is a fit to equation 2.14. The inset shows the plots of the measured suspension viscosities η vs. shear rate. The solid lines are fits to the Cross model (equation 2.13; fits are shown by black lines).

suspensions of soft colloidal particles can be estimated from the relation $\phi_{eff} = nV_d$ [19], where *n* is the number of particles per unit volume and $V_d = \pi(\langle d_h \rangle)^3/6$) is the volume of the undeformed particle of average hydrodynamic diameter $\langle d_h \rangle$ in a dilute suspension. The effective volume fraction estimation for soft deformable colloidal particles (PNIPAM, for example) in suspension is discussed below.

The viscosity η of aqueous PNIPAM suspensions is measured by varying shear rates $\dot{\gamma}$ between 0.001 to $4000s^{-1}$ using the double gap geometry (DG-26.7). Plots of η versus $\dot{\gamma}$ of PNIPAM suspensions having particle concentrations 1.0, 0.9 and 0.7 wt.% are shown in the inset of figure 2.7. The zero-shear viscosities η_0 of all the aqueous PNIPAM suspensions are estimated by fitting the η vs. $\dot{\gamma}$ curves with the Cross model [20]:

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + (k\dot{\gamma})^{\mathrm{m}}}$$
(2.13)

where η_0 and η_{∞} are the low and high shear rate viscosity plateaus respectively, k is a time constant related to the relaxation time of the macromolecules in aqueous suspension and m is a dimensionless exponent. The relative viscosity η_{rel} of an aqueous PNIPAM suspension is defined as the ratio of its zero-shear viscosity η_0 and the viscosity of water η_s : $\eta_{rel} = \eta_0/\eta_s$. The relative viscosity, η_{rel} , data is plotted vs. the polymer concentration, c, in figure 2.7. The data is fitted to Batchelor's equation [21, 22]

$$\eta_{rel} = 1 + 2.5(c/c_p) + 5.9(c/c_p)^2 \tag{2.14}$$

The effective volume fraction of PNIPAM particles in an aqueous suspension at a particular particle concentration can be estimated by extracting the parameter c_p , the polymer concentration inside each particle, from the fits to the Batchelor's equation, denoted by a solid line in figure 2.7. The effective volume fraction, ϕ_{eff} , of an aqueous soft colloidal suspension at a particular concentration, c, is related to the parameter c_p by the relation $\phi_{eff} = c/c_p$. The value of c_p is 12.18 wt.% for the present case and $\phi_{eff} = 1.9$ can be achieved by using c = 23.14 wt.% PNIPAM particles in aqueous suspensions.

2.4.1b. Oscillatory rheology

In oscillatory rheological measurements, a sinusoidal deformation (strain/stress) is applied to the sample and the corresponding response of the material (stress/strain) is measured. For example, if an applied oscillatory shear strain is given by:

$$\gamma(\omega) = \gamma_0 \sin(\omega t) \tag{2.15}$$

where γ_0 and ω are the amplitude of the applied oscillatory strain and angular frequency, respectively, then the corresponding stress response σ of the material at small strain amplitudes will be [23]:

$$\sigma(\omega) = \sigma_0 \sin(\omega t + \delta) \tag{2.16}$$

Here, σ_0 and δ are respectively the shear stress amplitude and phase lag. The value of δ will be zero for a purely elastic material (Hookean solid) and 90° for a purely viscous material (Newtonian liquids). For a viscoelastic material, δ lies between zero and 90°.

If a complex shear strain $\gamma^{\star} = \gamma_0 e^{i\omega t}$ is applied to the sample and the corresponding stress response $\sigma^{\star} = \sigma_0 e^{i\omega t+\delta}$ is measured, then the complex shear modulus $G^{\star}(\omega)$ of the material is given by [23]:

$$G^{\star}(\omega) = \frac{\sigma^{\star}}{\gamma^{\star}} = \frac{\sigma_0}{\gamma_0} e^{i\delta} = |G^*|(\cos(\delta) + i\sin(\delta)) = G'(\omega) + iG''(\omega)$$
(2.17)

where $G'(\omega)$ and $G''(\omega)$ are the elastic and viscous modulus of the sample respectively. The absolute value of the complex modulus can be writen as $|G^*(\omega)| = [G'(\omega)^2 + G''(\omega)^2]^{1/2}$. The ratio of the viscous and elastic moduli is known as the loss factor and is defined as $\tan(\delta) = G''(\omega)/G'(\omega)$ [23]. The oscillatory rheological measurement protocols that are used in this thesis work are discussed below.

2.4.1b(i). Strain amplitude sweep experiments

In strain amplitude sweep measurements, the viscoelastic moduli (G' and G'') of a sample are estimated by varying the amplitude of the applied sinusoidal strain (γ_0) at a constant angular frequency (ω). The strain amplitude sweep experiments are usually performed to study the extent of linearity of a viscoelastic sample. Figure 2.8 shows the strain amplitude sweep plot of a dense (10wt.%) aqueous PNIPAM suspension at 25°C. At small values of the applied strain amplitudes, G' and G''are independent of applied strain with G' > G''. This regime is characterized as the linear viscoelastic (LVE) regime. The sample starts yielding with an increase in applied strain amplitude which is characterized by a monotonic decrease in G',



Figure 2.8: Viscoelastic moduli, G' and G'' (represented by solid and open symbols in black respectively), and elastic stress, σ_{el} (red), of 10wt.% of aqueous suspension of PNIPAM particles at 25°C. The solid green line shows the fit of the elastic stress to Hooke's law [17]. The green horizontal and vertical dashed lines represent yield stress, σ_y , and yield strain, γ_y , respectively.

while G'' shows a peak before also decreasing. These are typical features of a soft glassy material, with the sample showing predominantly fluid-like characteristics, as indicated by G' < G'', at very high strain amplitudes.

To estimate the yield stress and strain of the material, the elastic stress, $\sigma_{el} = G' \times \gamma$, which separates the contribution of the elastic stress from the total stress, is plotted as a function of γ (figure 2.8). The value of σ_{el} at which the straight line fits $\sigma_{el} vs. \gamma$ deviates by more than 3% from the prediction of Hooke's law [17, 24], as indicated by the solid green straight line fit, is defined as the yield stress, σ_y , while the corresponding γ is the yield strain, γ_y .



Figure 2.9: Viscoelastic moduli, G' and G'' (represented by solid and open symbols respectively) of a 10wt.% aqueous PNIPAM suspension as a function of applied angular frequency at 25°C.

2.4.1b(ii). Frequency sweep experiments

In frequency sweep measurements, the angular frequency (ω) of the applied sinusoidal strain is varied, the strain amplitude (γ_0) is kept fixed and the corresponding viscoelastic moduli (G' and G'') of the sample are measured. These measurements are generally performed in the linear viscoelastic regime. Figure 2.9 shows the frequency sweep plot for a 10wt.% aqueous PNIPAM suspension at a fixed strain amplitude $\gamma_0 = 0.1\%$ and 25°C. The elastic modulus (G', solid symbol) of the sample displays frequency independent behavior while the viscous modulus (G'', hollow symbols) shows a minimum at a characteristic frequency. This behavior is a characteristic of a soft glassy sample, with the time corresponding to the minimum of G'' interpreted as signifying the structural relaxation time of the material. In the entire frequency range, G' dominates over G'', indicating the viscoelastic solid-like nature of this sample under the prevalent experimental condition.



Figure 2.10: Evolution of the elastic modulus G' and viscous modulus G'' with waiting time (time since preparation) t_w of a 2.8% w/v aqueous suspension of Laponite. Here, $t_w = 0$ is defined as the time at which stirring of the sample was stopped.

2.4.1b(iii). Time sweep experiments

Time sweep oscillatory experiments are performed to study systems whose properties evolve with time, such as aging systems. In these measurements, constant strain amplitude and frequency are applied to the sample and the time evolution of the viscoelastic moduli is measured. Figure 2.10 show the evolution of G' (filled symbols) and G'' (hollow symbols) with time of an aging 2.8% w/v aqueous Laponite suspension that was loaded in a double gap geometry (DG-26.7) just after preparation. It is seen that G'' dominates over G', immediately after preparation indicating viscoelastic liquid-like behavior. As time progresses, both moduli increase, with G'exceeding G'' at a transition time that indicates a crossover to viscoelastic solid-like behavior.



Figure 2.11: Elastic modulus G' (solid symbols) and viscous modulus G'' (open symbols) of a 20wt.% aqueous PNIPMAM suspension as a function of temperature T.

2.4.1b(iv). Temperature sweep experiments

In temperature sweep experiments, the viscoelastic moduli of the sample are measured by applying an oscillatory strain of constant amplitude and angular frequency while varying the sample temperature at a certain rate. Figure 2.11 shows the plots of G' and G'' as a function of temperature for a 20wt% aqueous PNIPMAM suspension, where the amplitude of strain γ_0 and angular frequency ω are kept constant at 0.1% and 1 rad/s respectively. It is seen that the viscoelastic moduli G' and G''change non-monotonically with increase in temperature. This typical mechanical behavior of a dense suspension of thermoresponsive PNIPMAM colloidal particles will be investigated and discussed in detail in Chapters 5 and 6.

2.5 Rheo-dielectric technique

The rheo-dielectric technique allows simultaneous measurements of rheological and dielectric properties of a material undergoing external shear deformation in the pres-


Figure 2.12: Photograph of our rheo-dielectric setup. A precision impedance analyzer is interfaced with a special parallel plate assembly in the Anton Paar MCR 702 rheometer.

ence of an electric field [25]. This technique can be used to study any material having permanent or field induced electrical dipoles [26]. In the rheo-dielectric technique, shear deformation is applied on a sample using a rheometer and its dielectric responses are measured using an impedance analyzer.

Figure 2.12 shows photographs of the different components of our rheo-dielectric setup. Here, the dielectric measurements are performed using a precision impedance analyzer (Wayne Kerr Electronics, 6500B series). An alternating electrical voltage of amplitude 750 mV over a frequency range between 20Hz and 5MHz is applied, and a stress-controlled Anton Paar MCR 702 rheometer is used to simultaneously apply oscillatory shears to the sample. A parallel plate sample geometry (PP-25/DI/TI) with a diameter of 25 mm and a measuring gap of 0.5 mm is used. The sample is sandwiched between the two plates that simultaneously serve as capacitor electrodes and shearing geometry (zoomed image in figure 2.12). In one of our experiments, oscillatory shear strains of amplitudes between 10% to 2000% at a fixed angular frequency of 10 rad/sec are applied to study the dielectric properties of aqueous PNIPAM suspensions under flow. The impedance analyzer is connected to the electrodes (top and bottom plates) with shielded wires. The measured capacitance (C) and loss factor (D) of the sample are used to estimate the real and imaginary

parts of the relative dielectric permittivities (ε'_r and ε''_r) using the equations: $\varepsilon'_r = C(d/A\varepsilon_0)$ and $\varepsilon''_r = D\varepsilon'_r$, where d, A and ε_0 are, respectively, the gap between the two electrode plates (0.5 mm in these experiments), the cross-sectional area of the top plate and the permittivity of free space.

2.6 SEM and cryo-SEM imaging techniques

Scanning electron microscopy (SEM) is a powerful technique to observe sample microstructures down to a few nanometers [27] and has been used extensively to study the microstructures of soft materials such as polymers, colloidal suspensions, hydrogels, biological samples, micellar solutions, etc [28–31]. SEM can be used to study sample microstructures in both dried and cryogenic states. In dry SEM, a dried sample is deposited on a conducting plate such as indium tin oxide (ITO) and in cryogenic scanning electron microscopy (cryo-SEM), a cryo-fractured sample coated with a thin metal layer is irradiated with a high-power electron beam. The backscattered or secondary electrons emitted from the sample are used to construct the surface microstructures of the sample.

A field effect scanning electron microscope (ULTRA-PLUS FESEM) from Carl Zeiss is used to study the sample's morphology. Figure 2.13 represents the schematic diagram of the main components of a typical SEM setup. It comprises an electron column, a scanning system, a detector, a vacuum system and a display unit [32]. The electron column of the SEM consists of an electron gun and two or more electromagnetic lenses operating in a vacuum. The free electrons that are generated from the electron gun can be accelerated to energies in the range of 1-100 keV [32]. Using a set of electromagnetic lenses containing copper coils that carry direct current and are enclosed in iron shrouds, an electron beam is focused to 1 nm on a specimen's surface [32]. Each surface point of the sample that is struck by accelerated electrons emits different types of electrons, such as backscattered electrons (BSE) and secondary electrons (SE). BSEs are, in fact, a part of the incident electrons which



Figure 2.13: Schematic diagram of a scanning electron microscopy (SEM) setup. This figure has been adapted from [32].

enter the sample and reflect back following elastic interaction between the electron beam and the sample. In contrast, SE originate from the sample's atoms due to inelastic interaction between the electron beam and the sample [32]. The yield of SE increases with decreasing angle between the incident beam and the sample surface [32]. Secondary electrons are distinguished from backscattered electrons by their much lower energies, typically a few electron volts [32].

In this thesis work, both secondary and backscattered electrons are used to study microstructures of the samples. The solid-state detector above the sample collects the backscattered electrons, while secondary electrons collected by the Everhart-Thornley detector are situated at an angle near the sample [32]. The output signal of the electron detector can be amplified and displayed on the screen of a synchronously



Figure 2.14: Scanning electron microscopy image of an aqueous PNIPMAM suspension in dry state.

scanned visual display unit such as a computer monitor [32]. The electron imaging in this thesis is performed using an electron beam of strength in the range of 2-5 KeV.

2.6.1 Sample preparation for SEM imaging

Glass plates coated with indium tin oxide (ITO) are used to scan the dried samples. The ITO substrate is cleaned with Milli-Q water and acetone. A suspension of colloidal particles is poured on the ITO-coated side of the substrate using a micro-pipette. The sample is then dried overnight at room temperature. The ITO substrate is loaded on the SEM stage for imaging. The electron beam interacts with the atoms of the sample. The backscattered secondary electrons are used to produce surface images of the samples. Data acquisition is performed using SmartSEM (software provided by Carl Zeiss) and ImageJ is used to analyze the SEM images. An SEM image of PNIPMAM particles in aqueous suspension in dry state is shown in figure 2.14.

2.6.2 Sample preparation for cryo-SEM imaging

The sample is first vitrified quickly in liquid nitrogen and then fractured before cryo-SEM imaging. This method helps in preserving the sample's microstructures. For aging samples such as aqueous Laponite suspensions, the samples are loaded in capillary tubes (Capillary Tube Supplies Ltd, UK) with bore sizes of 1 mm using capillary flow. The ends of the capillaries are sealed. Samples are kept undisturbed at room temperature before imaging and are then vitrified using liquid nitrogen slush at -190°C. Gel-like samples such as dense suspensions of PNIPAM particles are loaded in a ribett fixed with a cryo-stub and then freezed at -190° C by plunging into nitrogen slush at atmospheric pressure. Both the samples (samples in capillary tubes and ribett) are next sublimated for 5 minutes at a temperature of -90° C and then fractured with a stainless steel knife. The fractured samples are again sublimated for 15 minutes at -90°C to remove ice formed over the surface and then coated with a thin layer of platinum in vacuum conditions using a cryotransfer system (PP3000T from Quorum Technologies). The imaging of these samples is performed using a field-effect scanning electron microscope (FESEM), Ultra Plus FESEM-4098 from Carl Zeiss at an electron beam strength of 5 KeV. ImageJ (Java 1.8.0 172, developed by Wayne Rasband, NIH, US) is used to analyze the acquired images.

2.7 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a useful technique for studying heat transfer during physical and chemical processes. In DSC, differences in heat flow between a sample and reference are measured with changes in temperature or time, while the sample is continuously heated or cooled under controlled conditions. In this thesis work, differential scanning calorimetry (DSC) (Mettler Toledo, DSC 3) measurements are performed to estimate the lower critical transition temperatures (LCSTs) of aqueous suspensions of thermoresponsive microgels in dense aqueous suspensions.



Figure 2.15: Heat flow as a function of temperature for an dense aqueous PNIPAM suspension. The endothermic peak at 34.3°C corresponds to the LCST.

The temperature corresponding to the endothermic peak is characterized as the LCST of the thermoresponsive colloidal particles in aqueous suspensions. The heat flows estimated in the DSC experiments for a dense aqueous PNIPAM suspension is plotted in figure 2.15 as a function of temperature T. The temperature corresponding to the endothermic peak is characterized as the LCST of the PNIPAM particles in the aqueous suspension.

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Chapter 3

Influence of medium structure on the physicochemical properties of aging colloidal suspensions investigated using the synthetic clay Laponite[®]

3.1 Introduction

Physical aging in colloidal suspensions imposes dynamical constraints on the constituent particles leading to their kinetic arrest [1-3]. In charged colloidal suspensions, the physical aging dynamics and the subsequent changes in the physicochemical properties of the system are attributed to the growth of interparticle electrostatic interactions. Suspensions of charged clay colloids serve as excellent model candidates to investigate the aging dynamics and physicochemical properties of outof-equilibrium colloidal suspensions [4, 5]. The structure [1, 6], dynamics [7–10] and flow properties [11–15] of suspensions of smectite clay minerals have been studied extensively in the literature. Sodium-montmorillonite, also referred to as sodium Chapter 3. Influence of medium structure on the physicochemical properties of aging colloidal suspensions investigated using the synthetic clay Laponite[®] 71

bentonite, and kaolinite are two examples of clay minerals belonging to the smectite group that are available in abundance in nature [16]. The phases and bulk behaviors of smectite clay minerals can be easily tuned by tuning interparticle interactions. This has led to the widespread application of these clay minerals as rheological modifiers and stabilizers in paints, wellbore drilling fluids, cosmetics, pharmaceuticals, agrochemicals, paper fillers, coating pigments and nanocomposites [17–19]. In this chapter, we use aging aqueous suspensions of Laponite clay as a model system to investigate effects of solvent structure on the physicochemical properties of charged clay colloids. The aging dynamics and phase behavior of Laponite particles in aqueous suspensions are discussed in detail in section 1.5 of chapter 1.

Soil, in which clay is an important ingredient, and water are vital factors in sustaining life on earth. While water and salinity in soil influence the production of agricultural crops [20, 21], they also control large scale geophysical phenomena such as river delta formation, landslides and earthquake-driven liquefaction [22–24]. Na-montmorillonite nanoclay has been used as a model clay in laboratory experiments to study these geophysical phenomena [25]. Water is a structured medium in which pairs of water molecules engage in hydrogen bonding and arrange in tetrahedral configurations, the most energetically favored structure of liquid water [26, 27]. Extensive investigations of the effects of water content and salinity on the physicochemical properties of clay suspensions have been performed. However, to the best of our knowledge, the influence of water structure, manipulated by incorporating kosmotropic and chaotropic molecules in the suspension medium, has never been addressed in the literature. The contributions of interparticle electrostatic interactions, in contrast, have been extensively debated.

In this chapter, we focus our attention on the relative contributions of suspension medium structure and electrostatic interactions on the physicochemical properties of aging aqueous suspensions of a model hectorite clay mineral. To enhance the hydrogen bond population in liquid water, we incorporate glucose, a kosmotropic molecule (a molecule inducing structure formation in the aqueous medium) that forms dense layers of structured water around itself [28, 29]. In another experiment, we disrupt the water structure by adding N,N-Dimethylformamide (DMF), a chaotropic molecule (a molecule that disrupts the structure of the aqueous medium), to the suspension medium. DMF disrupts hydrogen bonding in liquid water by forming hydrogen bonds with the oxygen sites of DMF [30-32]. We disperse Laponite in aqueous solutions of glucose and DMF, prepared at different concentrations, to uncover the role of the structure of the suspension medium in determining suspension microstructure, dynamics and bulk flow properties. We hypothesize that since glucose and DMF are non-dissociating molecules, these experiments should reveal the influence of structure of the suspension medium on the physicochemical properties of clay suspensions. It is reported that the osmotic pressure of a solution strongly depends on the formation of hydration shells of water around the solute and on anion-cation interactions in ionic solutions [33, 34]. Since dense layers of water form around glucose molecules, osmotic pressure of the solution is enhanced [35, 36]. In contrast to glucose, DMF molecules disrupt the water structure and water molecules do not form hydration shells around DMF molecules. The incorporation of DMF therefore decreases the osmotic pressure of an aqueous solution [37]. It is wellestablished in the literature that osmotic pressure gradients drive suspension aging [4, 38]. By performing systematic dynamic light scattering (DLS) experiments, we report here that the presence of a kosmotropic molecule in solution accelerates the microscopic aging of clay suspensions, while suspension aging is retarded when a non-dissociating chaotrope is added.

While the addition of non-dissociating molecules reveals the role of suspension medium structure, ionic (dissociating) molecules that alter the local water structure can be employed to further evaluate the competition between suspension medium structure and electrostatic interactions on suspension properties. We implement this experimentally by adding two dissociating molecules, NaCl, a kosmotrope [30, 39, Chapter 3. Influence of medium structure on the physicochemical properties of aging colloidal suspensions investigated using the synthetic clay Laponite[®] 73

40], and KCl, a chaotrope, and study their effects on suspension properties through DLS and rheological studies. The action of NaCl and KCl on the local structure of water is described elsewhere [35, 39, 40]. Regardless of whether the dissociating molecules have a kosmotropic or chaotropic effect on the local structure of the suspension medium, an analysis of our DLS data reveals only accelerated suspension aging. We attribute this to the dominance of strong interparticle electrostatic interactions [5, 9] over changes in suspension medium structure in the presence of dissociating additives.

The microscopic dynamics uncovered from our dynamic light scattering studies are supported by rheological measurements. Particle-scale images are acquired using cryogenic scanning electron microscopy (cryo-SEM) and the morphologies of the observed suspension structures are quantified through measurements of average pore areas and network branch thicknesses. Regardless of the predominance of electrostatics or suspension medium structure on the properties of the suspensions, the microscopic aging dynamics are self-similar in the presence of all the additives explored here. We further report that viscoelastic moduli under large strains are sensitive to the presence of additives. The novelty of this study lies in the identification of the suspension medium structure as a key parameter in determining the physicochemical properties of Laponite suspensions. Our results can be generalized to other clay minerals belonging to the hectorite family whose aging dynamics are driven by osmotic pressure gradients.

3.2 Sample preparation and experimental techniques

Laponite XLG[®]powder (purchased from BYK Additives Inc., molecular weight-2286.9 g/mol) was dried in an oven at 120°C for 18 hours to remove moisture. The dried powder was weighed and added to Milli-Q water (Millipore Corp., resistivity



Figure 3.1: Normalized autocorrelation functions, C(t), vs. delay time, t, at 25°C for 12.2 mM (2.8% w/v) aqueous Laponite suspensions plotted for different suspension ages. The solid lines are fits to equation 3.1.

18.2 M Ω -cm) which was continually agitated using a magnetic stirrer for 45 minutes. The additives glucose (Sigma-Aldrich), DMF (SDFCL Fine Chem Pvt.Ltd), NaCl (LABORT Fine Chem Pvt.Ltd.), and KCl (Sigma-Aldrich) were measured and added to de-ionized water prior to the addition of Laponite powder. All the additives were used as received without any further purification. Dynamic light scattering (DLS) and rheology experiments in the presence of additives were performed at room temperature (25°C). Concentrations of the additives were chosen such that a complete decay of the auto-correlation function (ACF) could be recorded in the DLS experiments, while also ensuring that changes in suspension aging with changes in additive concentrations could be adequately resolved. The experimental techniques used in this chapter (DLS, rheology and cryo-SEM imaging) are discussed in detail in chapter 2.





Figure 3.2: Normalized autocorrelation functions, C(t), vs. delay time, t, at 25°C for (a) a 12.2 mM Laponite suspension and Laponite suspensions in the presence of (b) DMF (260 mM), (c) glucose (220 mM) at different scattering angles θ and at a waiting time $t_w = 100$ minutes. The solid lines are fits to equation 3.1.

3.3 Results and Discussions

Dynamic light scattering (DLS) experiments, were performed using a Brookhaven Instruments Corporation (BIC) setup whose details are given elsewhere [2, 5]. A glass cuvette filled with the suspension was held in a refractive index matching bath filled with decaline. For the DLS experiments, a freshly prepared sample was filtered into the glass cuvette through a Millipore filter of diameter 33 mm and pore size 0.45 μ m using a syringe. The increase in the sample waiting time, t_w , was monitored continuously from the time at which filtration was stopped $(t_w = 0$ at the completion of the filtration procedure). The decays of the normalized intensity autocorrelation functions, $C(t) = \frac{g^{(2)}(q,t)-1}{A}$, were measured for Laponite suspensions at different t_w . The normalized autocorrelation functions for 12.2 mM (2.8% w/v) aqueous Laponite suspensions at several t_w are plotted vs. delay time t in figure The normalized autocorrelation functions, C(t) plotted in figure 3.1, fit best 3.1. to functions representing two-step decays for the entire range of waiting times explored. This indicates the presence of two relaxation time-scales corresponding to two distinct dynamical processes. The fitting form that best describes C(t) is given by the following equation [2, 5, 41]

$$C(t) = [a \exp\{-t/\tau_1\} + (1-a) \exp\{-(t/\tau_{ww})^{\beta}\}]^2$$
(3.1)



Figure 3.3: The diffusive nature of the fast β - relaxation time, τ_1 , and mean slow α relaxation time, $\langle \tau_{ww} \rangle$ (left and right panels respectively), are shown for (a) a 12.2 mM Laponite suspension and Laponite suspensions in the presence of (b) DMF (260 mM), (c) glucose (220 mM) at different waiting times t_w . The solid lines are linear fits passing through the origin.

Fits equation 3.1 were used to extract τ_1 and τ_{ww} , identified as the time-scales associated with the β - and α - relaxation processes respectively. The faster β - relaxation involves the rattling motion of each particle inside its cage. The slower α - relaxation



Figure 3.4: Diffusion coefficients corresponding to β - (D_1) and slow α - (D_{ww}) relaxation processes for 12.2 mM aqueous Laponite suspensions and Laponite suspensions in the presence of 220 mM glucose and 260 mM DMF at $t_w = 100$ min. The inset shows D_1 and D_{ww} vs. waiting time t_w for 12.2 mM aqueous Laponite suspensions and Laponite suspensions in the presence of glucose and DMF.

corresponds to the time-scale at which the particle diffuses out of its cage in a process facilitated by the cooperative rearrangements of the surrounding particles. The parameters a and (1 - a) represent, respectively, the relative strengths of β - and α relaxation processes, while β in equation 3.1 is a stretching exponent that quantifies the distribution of the α - relaxation time-scales. The average α - relaxation time can be defined as $\langle \tau_{ww} \rangle = (\frac{\tau_{ww}}{\beta})\Gamma(\frac{1}{\beta})$ [42], where Γ is the Euler Gamma function. The present chapter studies the approach of Laponite suspensions towards kinetic arrest by systematically monitoring the evolution of the average α - relaxation time, $\langle \tau_{ww} \rangle$, with increasing sample waiting time, t_w , in the presence of several additives.

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Figure 3.2 shows the normalized intensity autocorrelation functions as a function of delay time, t, for a pure Laponite suspension and Laponite suspensions in the presence of DMF and glucose at different scattering angles θ and at a temperature $T = 25^{\circ}$ C. The straight line fits to the τ_1 and $\langle \tau_{ww} \rangle vs. 1/q^2$ plots in figure 3.3 pass through the origin and demonstrate the diffusive nature of both relaxation processes [43]. The reciprocal of the slope of each plot provides diffusion coefficients for both relaxation processes i.e. $D_1 = 1/\tau_1 q^2$ and $D_{ww} = 1/\langle \tau_{ww} \rangle q^2$, where D_1 and D_{ww} are the diffusion coefficients corresponding to β - (diffusion inside the cage) and α - (cooperative diffusion) relaxation processes respectively. The data is plotted in figure 3.4.

3.3.1 Microscopic aging dynamics in the presence of additives evaluated using dynamic light scattering

Figure 3.5 shows the evolution of the mean slow α - relaxation time $\langle \tau_{ww} \rangle$ with waiting time, t_w , estimated from fits of the DLS intensity autocorrelation data to equation 3.1, for 12.2 mM (2.8% w/v) aqueous Laponite suspensions (shown in magenta color symbols) at 25°C in the presence of different concentrations of dissociating and non-dissociating additive molecules in the suspension medium. We observe that when the concentration of glucose is increased, $\langle \tau_{ww} \rangle$ increases rapidly with increase in waiting time t_w (figure 3.5(a)). It is well known that aqueous Laponite suspensions age due to the swelling, exfoliation and rearrangement of Laponite particles/tactoids [11, 25, 38]. While cluster swelling is driven by osmotic pressure gradients, the subsequent exfoliation and rearrangement of Laponite particles are driven by interparticle electrostatic interactions [5, 9, 38]. Since glucose is a nondissociating molecule, the enhancement of suspension aging in the presence of glucose, manifested by the rapid time-evolution of $\langle \tau_{ww} \rangle$ (figure 3.5(a)), can be explained by considering the enhanced osmotic pressure gradients that are expected to arise due to the formation of tight hydration shells around glucose molecules [35, 36]. On the other hand, when DMF of different concentrations (shown in dark yellow



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Figure 3.5: Mean slow relaxation time $\langle \tau_{ww} \rangle vs$. waiting time t_w for 12.2 mM aqueous Laponite suspensions without and with different concentrations of additives (a) glucose (Glu), (b) DMF, (c) NaCl and (d) KCl. The solid lines are fits to equation 3.2. (e) The fitting parameters, t_{α}^{∞} (Vogel time) and $\langle \tau_{ww} \rangle^0$ ($\langle \tau_{ww} \rangle$ at $t_w \to 0$), of aqueous Laponite suspensions for different concentrations of additives. (f) Superposition of normalized mean slow relaxation times $\langle \tau_{ww} \rangle / \langle \tau_{ww} \rangle^0 vs$. normalized waiting times t_w/t_{α}^{∞} for aqueous Laponite suspensions without and with different concentrations of additives. All experiments are performed at $T = 25^{\circ}$ C.

symbols in figure 3.5(b)) is added to Laponite suspensions, the divergence of $\langle \tau_{ww} \rangle$ is delayed when compared to Laponite suspensions without any additives (shown in magenta color symbols). The addition of non-dissociating DMF molecules disrupts hydrogen bonds in water, with the water molecules forming hydrogen bonds with the oxygen sites of DMF [30–32]. This reduces the diffusion of bulk water molecules into the intra-gallery spaces of the Laponite tactoids and results in a reduction in osmotic pressure gradients and a retardation in the observed aging.



Figure 3.6: (a) Conductivity of 12.2 mM aqueous Laponite suspensions in the presence of different additives as a function of waiting time t_w . (b) Debye screening lengths (κ^{-1}) of pure 12.2 mM aqueous Laponite suspension and 12.2 mM Laponite suspensions in the presence of 1 mM NaCl and KCl as a function of waiting time t_w .

3.3.2 Electrostatic interactions dominate in the presence of dissociating additives, while suspension medium structure dominates in the presence of non-dissociating additives.

It is seen that when the concentrations of NaCl (shown in blue symbols in figure 3.5(c)) and KCl (shown in red symbols in figure 3.5(d)) in the suspension are increased, $\langle \tau_{ww} \rangle$ increases very rapidly with waiting time t_w . Figure 3.6(a) shows the conductivities of aqueous Laponite suspensions with and without additives. We estimated Debye screening lengths of aqueous Laponite suspensions from the data in figure 3.6(a) and the expression: $\kappa^{-1} = (\epsilon_0 \epsilon_r k_B T / \Sigma_i (z_i e)^2 n_i)^{1/2}$ [44], where ϵ_0 , ϵ_r , k_B , z_i , n_i and e are the permittivity of free space, relative permittivity, Boltzmann constant, valency of the *i*th ion, total number density of the *i*th ion and electron charge respectively. The Na⁺ ions in the Laponite suspensions are contributed by the externally added NaCl and the dissociation of Na⁺ from the Laponite surface. The concentration of Cl⁻ (which is contributed only by the added salt) can be computed from the concentration of the added salt. Concentration of Na⁺ can be calculated

using the relation: $\sigma = e(\mu_{Na}n_{Na} + \mu_{Cl}n_{Cl})$ [45], where σ is the conductivity of the system and mobilities of Na⁺ and Cl⁻ are given by μ_{Na} = $5.19\times10^{-8}~m^2/sV$ and $\mu_{Cl} = 5.19 \times 10^{-8} \ m^2/sV \ [46]$ respectively. In the presence of KCl, the concentration of Na⁺ can be estimated using: $\sigma = e(\mu_{Na}n_{Na} + \mu_{K}n_{K} + \mu_{Cl}n_{Cl})$, where mobility of $\mathrm{K^{+}}$ is $\mu_{K}=7.62\times10^{-8}~m^{2}/sV$ [46]. It is observed that the Debye screening lengths, κ^{-1} , of aqueous Laponite suspensions decrease continuously with waiting time (figure 3.6(b)). This indicates the continuous dissociation of sodium ions from the Laponite faces as the suspension ages. The addition of NaCl in the suspension medium leads to a further decrease in κ^{-1} (figure 3.6(b)), leading to an increase in the induced interparticle electrostatic attractions in the Laponite suspensions, presumably due to overlapping coin (OC) and house-of-cards (HoC) associations [47] of the Laponite platelets. The water molecules form tight hydration shells around Na⁺ [33], which enhances osmotic pressure gradients in the suspension. Increase in both interparticle electrostatic attractions and osmotic pressure gradients can potentially contribute to the observed acceleration in the aging of Laponite suspensions in the presence of NaCl (figure 3.5(c)). When KCl (widely regarded as a chaotrope and shown in red symbols) is added to the aqueous medium, the aging of the suspensions accelerate in spite of the chaotropic action of K⁺ on the suspension medium structure (figure 3.5(d)). The accelerated aging is attributed to a decrease in the Debye screening length (figure 3.6(b)) due to the participation of K⁺ ions in the EDLs surrounding the Laponite particles. Clearly, electrostatics drives suspension aging over kosmotropic or chaotropic action in the presence of dissociating additives. Our results are consistent with other works that report changes in the physicochemical properties of clay suspensions upon the addition of NaCl and KCl [48-50]. Despite the opposing actions of Na⁺ and K⁺ on the suspension medium structure, the dominance of electrostatic interactions on suspension aging is highlighted by these results.

Finally, to quantify the aging dynamics of clay suspensions without and with additives, we fit the data in figures 3.5(a-d) to the following equation [2, 5, 41]

$$<\tau_{ww}> = <\tau_{ww}>^{0} \exp\left[\frac{Dt_{w}}{t_{\alpha}^{\infty}-t_{w}}\right]$$
(3.2)

where D is the fragility parameter and $\langle \tau_{ww} \rangle^0$ is the mean α - relaxation time when $t_w \to 0$. The parameter t_{α}^{∞} is identified as the Vogel time or waiting time at which the suspension achieves a kinetically arrested state [2]. The time-scales t_{α}^{∞} and $\langle \tau_{ww} \rangle^0$ for aqueous Laponite suspensions with and without additives, extracted by fitting the data to equation 3.2, are plotted in figure 3.5(e). In figure 3.5(f), we superpose the $\langle \tau_{ww} \rangle$ vs. t_w data for all the suspensions (figures 3.5(a-d)) on a universal curve by dividing the horizontal and vertical axes by t_{α}^{∞} and $\langle \tau_{ww} \rangle^0$ respectively. The self-similar curvatures of the data indicate a common underlying mechanism in the aging of Laponite suspensions with and without additives. The observed increase in $\langle \tau_{ww} \rangle^0$ (shown in dark navy symbols in figure 3.5(e)) and the simultaneous decrease in t_{α}^{∞} (shown in dark purple symbols in figure 3.5(e)) in the presence of glucose, NaCl and KCl point to the increased confinement of Laponite particles in deep potential energy wells and a rapid acceleration in suspension aging. The addition of DMF, on the other hand, results in a decrease in $\langle \tau_{ww} \rangle^0$ and an increase in t_{α}^{∞} , indicating shallower potential wells and retarded aging.

Owing to the non-dissociating nature of glucose molecules, we see a decrease in the conductivity of the suspension in the presence of glucose (figure 3.6(a)). The enhanced aging of Laponite suspensions in the presence of glucose is therefore understood in terms of enhanced osmotic pressure gradients [35, 36] arising from the formation of hydration shells. It is seen from figure 3.5(b) that the addition of DMF delays suspension aging. Although DMF is known to be conducting [51], we conclude that the disruption of water structure upon the addition of DMF in Laponite suspensions dominates over any changes in interparticle electrostatics. Since glucose and DMF molecules do not participate in the EDL, these results establish the im-

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Figure 3.7: Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) vs. applied oscillatory strain amplitude γ for 12.2 mM aqueous Laponite suspensions at 25°C in the presence of different concentrations of additives (a) glucose (Glu), (b) DMF, (c) NaCl and (d) KCl at a waiting time $t_w = 200$ min. (e) Linear modulus and yield stresses, G'_l and σ_y , of Laponite suspensions without and with additives at $t_w = 200$ min. All experiments are performed at $T = 25^{\circ}$ C.

portance of structural changes in the suspension medium in determining suspension dynamics. EDLs of Laponite suspensions shrink in the presence of NaCl and KCl (figure 3.6(b)). While the present results confirm earlier observations of accelerated aging in the presence of NaCl [5, 9], we note here the same effect even in the presence of KCl, a dissociating chaotropic molecule. This observation is explained by considering the active participation of K⁺ in the EDL and the consequent dominance of electrostatic screening over any disruption of medium structure that the addition of KCl may have caused.



Figure 3.8: Viscoelastic moduli, G' and G'' (represented by solid and open symbols in blue respectively), and elastic stress, σ_{el} (red), of 12.2 mM aqueous Laponite suspensions in the presence of 2 mM NaCl at $t_w = 200$ min. The horizontal and vertical dashed lines represent yield stress, σ_y , and yield strain, γ_y , respectively.

3.3.3 Strong interparticle interactions result in structured suspensions with enhanced elasticities and yield stresses

We next perform oscillatory strain amplitude sweep rheology experiments to study the viscoelastic properties of aqueous Laponite suspensions with and without additives. In the strain amplitude sweep experiments we vary the strain amplitude, γ , from 0.1% to 500%, at a constant angular frequency, ω , of 6 rad/s. The viscoelastic moduli (elastic modulus G' and viscous modulus G'') of 12.2 mM aqueous Laponite suspensions ($t_w = 200$ min) with different concentrations of additives are plotted as a function of applied strain amplitude in figures 3.7(a-d). At small values of the strain (linear viscoelastic regime, LVE), G' and G'' of the suspensions are independent of the applied strain, with G' > G'' for all concentrations of added glucose, NaCl and KCl and for the samples with 50 and 90 mM DMF. The suspensions start Chapter 3. Influence of medium structure on the physicochemical properties of aging colloidal suspensions investigated using the synthetic clay Laponite[®] 85



Figure 3.9: Normalized (a) storage $(G'/G'_{0,5})$ and (b) loss $(G''/G''_{0,5})$ moduli vs. applied strain amplitude γ for aqueous Laponite suspensions with and without additives at $t_w =$ 200 min. Here, $G'_{0.5}$ and $G''_{0.5}$ are the values of the storage and loss moduli at strain 0.5%. The strain amplitude sweep data has been normalized following the procedure proposed in [52].

yielding with an increase in applied strain amplitude which is characterized by a monotonic decrease in G', while G'' shows a peak before also decreasing. These are typical features of soft glassy systems, with the suspensions showing predominantly fluid-like characteristics indicated by G'' > G' at very high strain amplitudes. In contrast, for Laponite suspensions with very high DMF concentrations (130 mM and 260 mM DMF in figure 3.7(b)), G'' > G' in the entire strain window, signifying liquid-like behavior at all strains.

In figure 3.7(e), we plot the linear modulus, G'_{I} (the magnitudes of G' extracted at very low applied strain amplitude γ , shown in violet symbols), and yield stresses, σ_{ν} (shown in wine symbols), of aqueous Laponite suspensions with and without additives at $t_w = 200$ min. The yield stresses are calculated from strain amplitude sweep data following the method proposed by Laurati et al. [53]. The details of the analysis is described in section 2.4.1b(i) of chapter 2 and a representative plot is shown in figure 3.8. Both G'_l and σ_y , which estimate the strength of the underlying sample microstructures [47], increase with increasing concentrations of glucose, NaCl and KCl, and decrease with increasing DMF concentration. In figure 3.9, we normalize the storage and loss moduli data measured in oscillatory strain amplitude sweep



Figure 3.10: Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) vs. t_w for 12.2 mM aqueous Laponite suspensions in the presence of different concentrations of additives (a) glucose, (b) DMF (Glu), (c) NaCl and (d) KCl. (e) The transition time t_r at which a viscoelastic liquid transforms to a viscoelastic solid (time at which G' = G'') for Laponite suspensions with and without additives.

rheological experiments by dividing the moduli at different strain amplitudes with those measured at a strain ($\gamma = 0.5\%$) in the LVE regime [52]. As expected, the microscopic dynamics and rheological responses in the limit of low strains collapse well. In contrast, the mechanical responses of Laponite suspensions at high strains are sensitive to the presence of additives.

Figures 3.10(a-d) show the evolution of the storage and loss moduli (G' and G'') with waiting time t_w for aqueous Laponite suspensions without and with additives. Soon after preparation, G'' dominates over G' for all the suspensions, thereby indicating viscoelastic liquid-like behavior. As time progresses, both moduli increase, with G' exceeding G'' at a transition time, t_r . The transition times, t_r , at which the viscoelastic liquid transforms to a viscoelastic solid are plotted in Figure 3.10(e). It is observed from this figure that the transition of aqueous Laponite suspensions from viscoelastic liquid to viscoelastic solid occurs earlier when the kosmotropes, glucose



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Figure 3.11: Representative cryo-SEM micrographs for (a) a 12.2 mM aqueous Laponite suspension and Laponite suspensions in the presence of (b) 90 mM glucose, (c) 90 mM DMF, (d) 1 mM NaCl and (e) 1 mM KCl at $t_w = 24$ hours. (f) Average pore area (black) and linear modulus (red) for aqueous Laponite suspensions without and with additives at $t_w = 24$ hours. The error bars for the average pore areas include information on pore size polydispersity.

and NaCl, and the chaotrope KCl are added to the suspension. In contrast, the transition is retarded when the chaotrope DMF is added. The rheological results are therefore consistent with the DLS results (figure 3.5) reported earlier.



Figure 3.12: Magnified cryo-SEM micrographs for (a) a 12.2 mM aqueous Laponite suspension and Laponite suspensions with (b) 90 mM glucose, (c) 90 mM DMF, (d) 1 mM NaCl and (e) 1 mM KCl at $t_w = 24$ hours. OC refers to overlapping coin configurations of Laponite platelets.



Figure 3.13: Network branch thickness for 12.2 mM Laponite suspensions with and without additives at $t_w = 24$ hours.

3.3.4 Decrease in average pore area of the self-assembled suspension structures increases suspension elasticity

We perform cryo-SEM experiments to investigate the morphologies of the samples studied here. The details of cyro-SEM imaging is described in section 2.6 of chapter 2. Figures 3.11(a-e) display the microstructures of aqueous Laponite suspensions without and with additives at a waiting time $t_w = 24$ hours. Honeycomb like network structures are seen in all samples, with pore sizes that are sensitive to the additive nature and concentration. We note the existence of holes on the flat surfaces of the network branches, indicating the possibility of overlapping coin configurations (OC) [54] of the Laponite platelets [47]. The magnified cryo-SEM micrographs of the sample microstructures are displayed in figure 3.12.



Figure 3.14: Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) as a function of applied strain amplitude γ for 12.2 mM aqueous Laponite suspension in the presence of different additives at $t_w = 24$ hours. G'_l , the linear modulus, is extracted for all the samples by estimating G' ($\gamma \to 0$).

We adopt a protocol used earlier [47] to quantify the porous microstructures by estimating average pore areas (data at $t_w = 24$ hours is shown in black symbols in figure 3.11(f)) and branch thicknesses (figure 3.13). In the analysis of cryo-SEM images, the presence of vitrified water on the structures can lead to an overestimation of the network branch thickness and a simultaneous underestimation of average pore area. However, since the sublimation time after cutting the vitrified samples (15 minutes) is identical in all the experiments, an equal sublimation-depth is expected for all the samples studied using cryo-SEM. We next correlate network morphologies with their mechanical responses obtained in rheological experiments. The linear modulus, G'_l (magnitude of G' of all the samples at $t_w = 24$ hours extracted at very low applied strain amplitude γ (figure 3.14)), are plotted in figure 3.11(f) (shown in red symbols). While the branch thicknesses of the samples remain unchanged in all the samples studied here, the average pore area decreases



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Figure 3.15: Cryo-SEM micrographs for (a) a 12.2 mM aqueous Laponite suspensions without additives and with (b) 90 mM glucose, (c) 90 mM DMF, (d) 1 mM NaCl and (e) 1 mM KCl at $t_w = 200$ minutes. (f) Average pore area for 12.2 mM aqueous Laponite suspensions in the presence of 90 mM glucose, 1mM NaCl and 1 mM KCl at waiting times 24 hours (black) and 200 minutes (olive).

for Laponite suspensions in the presence of glucose (\blacklozenge) , NaCl (\blacktriangle) and KCl (\spadesuit) . Figure 3.11(f) displays a simultaneous increase in the elasticity of these samples. In contrast, an increase in average pore area and a simultaneous decrease in elasticity is noted when DMF of concentration 90 mM (black circle in figure 3.11(f)) is added to Laponite suspensions. Many small dangling branches are observed at the walls of

the sample microstructures in figure 3.11(c), which indicates incomplete structure formation and retarded aging in the suspension with DMF. In figure 3.15, we show the microstructures of aqueous Laponite suspensions in the presence of different additives at $t_w = 200$ minutes. When glucose, NaCl and KCl are added to Laponite suspensions, network structures, with average pore areas larger than those observed in the same samples at a longer waiting time ($t_w = 24$ hours, figure 3.11), are noted (figure 3.15(f)). This indicates the continual aging of the suspension structures. The cryo-SEM data establishes that the suspensions with smaller average pore sizes are characterized by higher elasticities (obtained from rheological measurements) which further correlates with the microscopic aging dynamics measured using DLS. Clearly, aqueous Laponite suspensions age faster in the presence of dissociating molecules such as NaCl and KCl due to the dominance of interparticle electrostatic interactions over alterations in the suspension medium structure. The contribution of water structure dominates only in the case of non-dissociating molecules, with the kosmotropic glucose and the chaotropic DMF respectively causing acceleration and delay in suspension aging.

3.4 Conclusions

This chapter identifies the suspension medium structure as one of the key control parameters that determines the physicochemical properties of aqueous colloidal suspensions of charged nanoclay particles. An enhancement in hydrogen bond population in the medium by adding non-dissociating kosmotropic molecules accelerates the suspension aging, increases the elastic modulus of the sample and reduces the network pore sizes of the suspension structures. In contrast, addition of nondissociating chaotropic molecules disrupts the medium structure, delays the aging, reduces the elastic modulus and increases the network pore sizes. Furthermore, we note that interparticle electrostatic interactions determine suspension properties in the presence of dissociating molecules, suppressing the contribution of the local structure of the suspension medium. Our inferences on the particle dynamics are in agreement with the rheological properties of the samples and correlate well with the microstructural details of the suspensions visualized using cryogenic scanning electron microscopy.

Moelbert et al. [55] and Shiraki et al. [56] have reported that aggregation of hydrophobic solutes is promoted by kosmotropes while the aggregates are destabilized in the presence of chaotropes. This observation also holds true for amorphous aggregates. It was seen that the addition of kosmotropes enhances the fusion temperature of poly(vinyl alcohol) cryogels, while the addition of chaotropic molecules reduces their rigidity [57]. Morales *et al.* [58] identified that kosmotropic substances stiffen the protein-hydration layer system while chaotropes soften this layer. In our study, we observe enhanced rigidity of Laponite suspensions when glucose, a non-dissociating kosmotropic molecule, is added to the suspension medium. We also report a reduction in sample rigidity when DMF, a non-dissociating chaotropic molecule (N,N-dimethylformamide), is added. Ionic, dissociating molecules like NaCl and KCl induce strong electrostatic interactions between clay particles and reduce the influence of local structure of the suspension medium in determining sample properties. Despite the crucial roles of soil water content and salinity in agriculture and large scale geophysical phenomena such as river delta formation and landslides, a laboratory scale experimental investigation on the influence of water structure on the physicochemical properties of aqueous clay colloidal suspensions has never been considered before.

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Chapter 4

Study of aging dynamics of aqueous suspensions of clay particles with different thermal histories

4.1 Introduction

Laponite[®] is a synthetic clay, which when dispersed in water, shows a variety of phases that depend on clay concentration. The phase behavior [1–5], rheological properties [6–9] and aging dynamics [9–11] of aqueous Laponite suspensions, widely investigated in the literature, are very sensitive to the presence of additives such as acid and salt, suspension temperature, applied electric field and preparation protocol. The sensitivity of Laponite microstructures, and the rheology and aging dynamics of their suspensions have been investigated in chapter 3. As discussed previously, Laponite suspensions with concentrations above 2wt.% display physical aging [10, 12, 13]. The mechanism of aging of aqueous Laponite suspensions and their phase behavior are discussed in section 1.5 of chapter 1. A non-monotonic evolution of the mechanical strength of acid induced Laponite gels, whose aging Chapter 4. Study of aging dynamics of aqueous suspensions of clay particles with different thermal histories 103

behavior is driven by osmotic swelling, is observed with sample waiting time t_w [14]. It has been shown that aqueous Laponite suspensions rapidly transform into soft solids when DC electric fields are applied [15]. Laponite is an excellent rheology modifier and is often used in cosmetics, pharmaceutical products, food industries, etc [16]. Aqueous suspensions of Laponite have been used as a replacement for natural clays for modeling large scale geophysical phenomena involving soil suspensions such as in river delta formation and landslides [17, 18]. It is reported that the sizes of cooperatively rearranging regions of dynamical heterogeneities in Laponite suspensions increase monotonically with increasing waiting time t_w and clay concentration C_L [19]. Moreover, aqueous Laponite suspensions can be used as model glass formers to study the physics of the glass transition [20–22].

In this chapter, we use temperature as a control parameter to disrupt hydrogen bonds in liquid water. The hydrogen bond population in the medium is manipulated through temperature controlled experiments that enforce two different thermal histories as described below. In the first method, we fix the temperature of the suspension medium to a pre-selected target value prior to the addition of Laponite particles. We refer to these experiments as prefixed temperature experiments. In the second method, designated as postfixed temperature experiments, we set the temperature immediately after loading the suspension, prepared at room temperature, in the experimental setup. Besides disrupting hydrogen bonds, an increase in the temperature of aqueous Laponite suspensions shrinks the electrical double layer due to an increase in the number of dissociated Na^+ ions in the medium [22]. For studies conducted above room temperature, an enhancement in suspension aging is observed in the prefixed temperature experiments when compared to the postfixed temperature ones. Our experiments confirm that when temperature is varied, electrostatic interactions dominate over changes in the local structure of the suspension medium in determining the physicochemical properties of aging suspensions of charged clay colloids. The microscopic dynamics of Laponite particles in aqueous suspensions are studied using dynamic light scattering and are supported by rheological measurements. Regardless of the different thermal histories, the microscopic aging dynamics are self-similar for all suspension temperatures explored here. We further report that viscoelastic moduli under large strains are sensitive to temperature histories.

4.2 Sample preparation and experimental techniques

Laponite XLG[®]powder (purchased from BYK Additives Inc., molecular weight-2286.9 g/mol) was dried in an oven at 120°C for 18 hours to remove moisture. The dried powder was weighed and added to Milli-Q water (Millipore Corp., resistivity 18.2 M Ω -cm) which was continually agitated using a magnetic stirrer for 45 minutes. Experiments at different suspension temperatures were performed following two different protocols. In the first protocol, which we refer to as prefixed temperature experiments, the temperature of the water was set to a pre-selected target value before the addition of Laponite powder and was maintained throughout the stirring time (45 minutes). In the second protocol, which we have labelled as postfixed temperature experiments, the temperature of the suspension was changed to a pre-selected target value after loading the suspension, prepared at room temperature, in the experimental setup. The experimental techniques used in this chapter (DLS and rheology) are discussed in detail in chapter 2.

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Figure 4.1: Normalized autocorrelation functions, C(t), vs. delay time, t, plotted for different suspension ages at temperatures (a) 15°C (b) 35°C and (c) 55°C for prefixed temperature experiments. The solid lines are fits to equation 3.1.

4.3 **Results and Discussions**

4.3.1 Electrostatics, rather than hydrogen bond populations, determines suspension aging in temperature-controlled experiments

Representative plots of intensity autocorrelation functions C(t) vs. t for aqueous Laponite suspensions at three different temperatures are shown in figure 4.1. The fits of the data to equation 3.1 are shown by solid lines. Figure 4.2(a) plots the dependence of the mean slow α - relaxation time, $\langle \tau_{ww} \rangle$ on t_w and the fits of the data to equation 3.2 for both prefixed and postfixed experiments. We observe that higher suspension temperatures result in accelerated aging. The kosmotrope-like effect (discussed in chapter 3) of temperature on the suspension aging dynamics in postfixed temperature experiments has been reported in an earlier work [22]. Figure 4.3(a) shows the conductivity of aqueous Laponite suspensions at different temperatures. We estimated Debye screening lengths of aqueous Laponite suspensions following the methods described in chapter 3. We note that while increasing temperature disrupts hydrogen bonds, there is a simultaneous enhancement in the interparticle electrostatic attraction, arising due to decrease in the Debye screening length κ^{-1} (figure 4.3(b), calculated from conductivity measurements plotted in fig-



Figure 4.2: (a) Mean slow relaxation time $\langle \tau_{ww} \rangle vs$. waiting time t_w for prefixed and postfixed temperature experiments, with target temperatures between 15°C and 55°C, for aqueous Laponite suspensions of concentration 12.2 mM. The solid lines are fits to equation 3.2. (b) Superposition of normalized mean slow relaxation times $\langle \tau_{ww} \rangle \langle \tau_{ww} \rangle^0 vs$. normalized waiting times t_w/t_{α}^{∞} . (c) Horizontal and vertical shift factors, t_{α}^{∞} (Vogel time) and $\langle \tau_{ww} \rangle^0$, for suspensions with prefixed and postfixed temperatures.



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Figure 4.3: (a) Conductivity of prefixed and postfixed 12.2 mM aqueous Laponite suspensions as a function of t_w . (b) Debye screening lengths (κ^{-1}) of suspensions with prefixed and postfixed temperatures as a function of t_w .

ure 4.3(a)). At high enough temperatures, therefore, electrostatics can be expected to dominate over disruption in medium structure while determining suspension dynamics. Interestingly, we observe a comparatively more rapid enhancement in the aging of aqueous Laponite suspensions, prepared at above room temperatures, in prefixed temperature experiments (figure 4.2(a)). The enhanced aging in these samples, when compared to the postfixed scenario, arises from the larger decrease in Debye screening lengths in the former case (figure 4.3(b)) due to an increased dissociation of Na⁺ in the former experimental protocol. A steady dependence of the Debye screening length κ^{-1} on waiting time t_w is achieved in postfixed temperature experiments only after an initial time interval, which is approximately 5 minutes in our studies (figure 4.3(b)). Since in the prefixed temperature experiments, the temperature of the suspension medium was already fixed beforehand, we do not observe a significant variation of κ^{-1} in the initial time interval as reported by us for the postfixed temperature experiments.

The superposition plot of the $\langle \tau_{ww} \rangle$ data (figure 4.2(b)) shows self-similar behavior, thereby revealing an indistinguishable aging mechanism of aqueous Laponite suspensions for all thermal histories. The horizontal and vertical shift factors, t_{α}^{∞}



Figure 4.4: (a) Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) vs. applied oscillatory strain amplitude γ for prefixed and postfixed temperature experiments, with target temperatures in the range between 15 and 55°C with aqueous Laponite suspensions at $t_w = 200$ minutes. (b) Linear modulus and yield stresses, G'_l and σ_y , of Laponite suspensions at $t_w = 200$ minutes for temperatures in the range 15-55°C both for prefixed and postfixed temperature experiments.

and $< \tau_{ww} >^0$ (extracted by fitting the data in figure 4.2(a) to equation 3.2), are plotted in figure 4.2(c). The observed decrease in t_{α}^{∞} (displayed in figure 4.2(c) using blue symbols) with increase in suspension temperature indicates accelerated aging due to enhancement in structural buildup in the suspensions in both prefixed and postfixed experimental scenarios. However, in these two sets of experimental protocols, we observe an inverse trend in $\langle \tau_{ww} \rangle^0$ (defined as $\langle \tau_{ww} \rangle$ at $t_w \to 0$) below and above room temperature. Following the protocol outlined above for the postfixed temperature experiments, we disperse Laponite powder in water before we cool the sample to 15°C. The number of counter ions in this sample is therefore higher than that in samples with prefixed temperatures. The larger number of Na⁺ counter ions at 15° C for postfixed temperature experiments accelerates inter-Laponite attractive interactions and results in higher $\langle \tau_{ww} \rangle^0$ (\triangleright) when compared to samples with prefixed temperatures (**•**). For experiments performed above room temperature $(25^{\circ}C)$, heating the suspension medium to a pre-selected target temperature before addition of Laponite (prefixed temperature experiments) results in accelerated leaching of sodium ions when compared to the experiments with temperatures fixed later (postfixed). This is consistent with our conductivity measurements shown in figure 4.3(a). Therefore, $\langle \tau_{ww} \rangle^0$ is consistently larger in prefixed temperature experiments when compared to postfixed temperature experiments, for the DLS experiments conducted above room temperature. These measurements demonstrate that despite manipulation of the hydrogen bonds of liquid water using two different approaches, electrostatic interactions, rather than hydrogen bond populations, determine the physical properties of the suspensions regardless of their temperature histories.

Next, oscillatory strain amplitude sweep rheological experiments are performed to study the viscoelastic behavior of aqueous Laponite suspensions at different temperatures. Figure 4.4(a) shows the temperature dependence of the viscoelastic moduli (G' and G'') of 12.2 mM aqueous Laponite suspensions at $t_w = 200$ minutes as a function of applied strain amplitude, $\gamma.$ The linear moduli, G_l' (olive symbols), and yield stresses, σ_{y} (orange symbols), of aqueous Laponite suspensions increase with temperature (figure 4.4(b)) which indicate enhanced rates of structure buildup [23] and accelerated aging. The higher G'_{l} and σ_{v} values at higher temperatures obtained in the prefixed temperature experiments when compared to postfixed temperature experiments confirm faster aging in the former case and are in agreement with the results of the DLS experiments reported in figure 4.2. Similar to observations in Laponite suspensions in the presence of additives, we note that while the microscopic dynamics (figure 4.2(a)) and linear rheological responses collapse well at all temperatures (except the rheological strain amplitude sweep data at 15°C for the sample with prefixed temperature), the nonlinear mechanical responses are sensitive to temperature histories over the experimental strain window (figure 4.5). We conclude that even though increase in temperature disrupts hydrogen bonds in the suspension medium, the enhancement in interparticle electrostatics due to increased dissolution of Na⁺ from the Laponite particles dominates suspension dynamics. While the kosmotrope like effect of temperature has been demonstrated



Figure 4.5: Normalized (a) storage $(G'/G'_{0.5})$ and (b) loss $(G''/G''_{0.5})$ moduli vs. applied strain amplitude γ for prefixed and postfixed suspensions at $t_w = 200$ min. $G'_{0.5}$ and $G''_{0.5}$ are the values of the storage and loss moduli at strain 0.5%.

before [9, 22], comparisons of the effects of prefixing and postfixing the temperature on suspension properties have never been reported in the literature to the best of our knowledge.

4.4 Conclusions

In this chapter, we investigated the aging dynamics of aqueous Laponite suspensions with two different thermal histories, referred to as prefixed and postfixed temperature experiments. In prefixed temperature experiments, the temperature of the suspension medium is fixed before the addition of Laponite particles. In postfixed temperature experiments, in contrast, the sample is prepared at room temperature and its temperature is raised to a pre-selected target value after loading in the experimental setup. For both prefixed and postfixed experiments performed above room temperature, the effects are reminiscent of those arising from the incorporation of ionic additives at room temperature. Increase in suspension temperature accelerates the dissociation of Na⁺ counterions and enhances interparticle electrostatic attractions. The enhanced interparticle electrostatic interactions at higher temperatures dominate over changes in solvent structure and give rise to accelerChapter 4. Study of aging dynamics of aqueous suspensions of clay particles with different thermal histories 111

ated aging. Our results are in agreement with previous studies that reported the influence of electrostatic interactions and suspension temperatures on suspension dynamics [21, 22, 24–26]. The conclusions reported in this chapter are sufficiently general and can be extended to suspensions of other charged clays, for example, sodium bentonite and kaolinite, whose aging dynamics are determined by a combination of local osmotic pressure gradients and electrostatic interactions.

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Chapter 5

Influence of particle size on the thermoresponsive and rheological properties of aqueous poly(*N*-isopropylacrylamide) colloidal suspensions

5.1 Introduction

Thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) particles, suspended in an aqueous medium, can swell and deswell in response to changes in the temperature of the medium [1]. PNIPAM particles in aqueous suspensions undergo a reversible volume phase transition above the lower critical solution temperature (LCST) of \approx 34° C [1, 2]. Below the LCST, PNIPAM particles absorb water and swell. Above the LCST, however, they become hydrophobic and expel water which results in dramatic shrinkage in their sizes [3]. As a result of this thermoresponsive behavior, PNIPAM particles offer an advantage over many temperature insensitive hard particles like polystyrene and PMMA. The volume fraction of PNIPAM particles in an aqueous suspension can be tuned by changing the temperature of the medium without changing the particle number density [4, 5]. An important consequence of the deformability and compressibility of soft microgel particles is that model microgels, such as aqueous PNIPAM suspensions, can be packed well above the random close packing fraction of monodisperse hard spheres, $\phi_{rcp} \approx 0.64$. Due to their thermoresponsive properties and deformability, PNIPAM particles have been widely used in many applications like drug delivery [6, 7] and as bio-sensors [8]. Moreover, dense aqueous suspensions of PNIPAM particles can be used as model systems to study the structures and dynamics of the kinetically arrested states of dense colloidal suspensions [9, 10].

The temperature dependent phase behavior of dense aqueous PNIPAM suspensions has been studied extensively [11–13]. It has been reported that below the LCST, PNIPAM particles swell and interact repulsively. The interaction between the particles changes from repulsive to attractive with increase in temperature above the LCST [13]. An interesting consequence of this property is that as the temperature is increased beyond the LCST, the particles aggregate and assemble into a gel phase [14, 15]. PNIPAM particles in dense aqueous suspensions can therefore undergo a reversible phase transition from a glassy to a gel-like state while passing through an inter-mediate liquid-like state.

The thermoresponsive and rheological behaviors of PNIPAM colloidal particles have been extensively investigated by varying the stiffness of the PNIPAM particles [15–17]. This has been achieved experimentally by varying the concentration of the crosslinker N, N'-methylenebisacrylamide (MBA) during the synthesis process [18, 19]. It has been reported that stiff PNIPAM particles in dense aqueous suspension exhibit a phase transition from a liquid to a glassy state while passing through an intermediate crystalline phase with increase in the particle volume fraction. Particles with intermediate stiffnesses, in contrast, transform to a glassy state from a liquid state directly without passing through a crystalline phase [16]. Soft PNIPAM particles suspended in water, however, remain in a liquid phase for the entire range of volume fractions explored in these experiments. The stiffness of the PNIPAM particles significantly affects the mechanical behavior of these particles in dense aqueous suspensions. It was observed that the plateau of the elastic modulus of dense aqueous PNIPAM suspensions becomes weaker when the stiffness of the particles is decreased [19]. This is because a higher crosslinking density leads to a higher interparticle force. Another way of changing the particle stiffness is by varying the concentration of the surfactant, sodium dodecyl sulfate (SDS), during the synthesis process [18, 20]. It was reported that an increase in SDS concentration leads to decrease in size of the PNIPAM particles in aqueous suspensions [20]. SDS adsorbs on the surface of the primary particles during the nucleation process. This increases the colloidal stability of the particles and decreases the size of the particles.

In this chapter, we report the influence of particle size on the thermoresponsive and rheological properties of PNIPAM particles in aqueous suspensions. The rheology of jammed suspensions of these particles is interesting because of our ability to control the particle stiffnesses, which in turn, alters the packing properties of their dense suspensions. No studies in the literature, to the best of our knowledge, connect particle stiffness, varied by varying SDS concentration, to bulk / macroscopic properties such as rheology.

In the present chapter, PNIPAM particles of different sizes are synthesized by varying the sodium dodecyl sulfate (SDS) concentration in the one-pot free radical precipitation polymerization method [10, 18]. The sizes and size distributions of PNIPAM particles are estimated using dynamic light scattering (DLS) and scanning electron microscopy (SEM). The size distribution of PNIPAM particles in aqueous suspensions has been characterized by a dimensionless polydispersity index (PDI). Differential scanning calorimetry (DSC) experiments are performed to characterize the LCSTs of PNIPAM particles of different sizes and stiffnesses in aqueous suspensions. Crosslinker densities (CLDs) of PNIPAM particles in aqueous suspensions are estimated using a statistical model for the Helmholtz free energies of these microgels. Moreover, temperature sweep oscillatory rheological measurements are performed to study the viscoelastic and thermoresponsive behaviors of these suspensions. Finally, we connect the bulk rheology of these suspensions to the stiffnesses of individual particles in aqueous suspensions.

5.2 Sample preparation and experimental methods

Poly(*N*-isopropylacrylamide) (PNIPAM) particles are synthesized using one-pot free radical precipitation polymerization method (discussed in detail in section 2.2.2 of chapter 2), and the condition for the synthesis of PNIPAM particles used in this chapter are tabulated in table 5.1. After synthesis, the suspensions are purified by 4 successive centrifugation and re-dispersion procedures to remove SDS, the excess monomers, oligomers and other impurities. Centrifugations are performed at speeds of 20,000-55,000 RPM for 60 minutes. After the centrifugation, the supernatant is removed and the remaining sample is dried by evaporating the water. A fine powder is prepared by grinding the dried particles with a mortar and pestle. For dynamic light scattering measurements and scanning electron microscopy images, very dilute aqueous PNIPAM suspensions are prepared by adding dried PNIPAM powder in Milli-Q water. For rheological measurements, concentrated aqueous suspensions of PNIPAM particles are prepared by adding dried PNIPAM powder in Milli-Q water. The suspension is then stirred for 24 hours and sonicated for 30 minutes. The concentrated suspension is next diluted to prepare PNIPAM suspensions of different concentrations. Since PNIPAM particles are soft and deformable, the volume fraction ϕ is not an appropriate measure to quantify their packing in aqueous suspensions. Therefore, a modified parameter called effective volume fraction, ϕ_{eff} , is used. Figure 5.1 shows the plot of relative viscosity as a function of particle concentration for aqueous suspensions of PNIPAM particles synthesized using different

NIPAM	MBA	KPS	S DS	$d_{25^oC}(nm)$	PDI(%)	$\alpha(d_{fullswell}/d_{fullshrunk})$
14	1.4	0.56	0.01	600	10.29	≈1.49
14	1.4	0.56	0.06	450	9.15	≈1.63
14	1.4	0.56	0.15	270	8.31	≈1.71
14	1.4	0.56	0.3	155	8.96	≈1.80
14	1.4	0.56	0.6	125	8.68	≈1.87

Table 5.1: Summary of synthesis conditions used for the synthesis of PNIPAM particles by the free radical precipitation polymerization method and the properties of the synthesized particles. The concentrations of monomer (NIPAM), crosslinker (MBA), initiator (KPS) and surfactant (SDS) are expressed in g/L. All the syntheses are performed in 200 mL volumes.

concentrations of SDS. The protocol for estimating the effective volume fractions of PNIPAM particles in suspension is discussed in detail in section 2.4.1a(i) of chapter 2. The estimated effective volume fractions and the corresponding concentration of PNIPAM particles in aqueous suspensions for three different maximum swelling ratios 1.87, 1.71, and 1.49 are listed in table 5.2. Experimental techniques used in this chapter (DLS, rheology, SEM and DSC) are described in detail in chapter 2.

5.3 Results and discussion

The average sizes, size distributions, and thermoresponsivity of PNIPAM particles in dilute aqueous suspensions are quantified using dynamic light scattering (DLS) measurements. The details of the setup and protocol for estimating sizes of colloidal particles are discussed in section 2.3 of chapter 2. The size distributions of PNIPAM particles in aqueous suspensions, obtained from DLS data using the CONTIN algorithm [21, 22], are quantified by a dimensionless polydispersity index (PDI) which is defined as the ratio of the standard deviation or width of the particle size distribution, $\sigma = \frac{k_B T \sqrt{\langle \tau^2 \rangle - \langle \tau \rangle^2} q^2}{3\pi \eta}$, and the average hydrodynamic diameter ($\langle d_H \rangle$) of the particle. The mean relaxation time, $\langle \tau \rangle$, and the second moment of the relaxation time spectrum, $\langle \tau^2 \rangle$, of the particles in suspension can be calculated using the relations, $\langle \tau \rangle = (\frac{\tau}{\beta})\Gamma(\frac{1}{\beta})$ and $\langle \tau^2 \rangle = (\frac{\tau^2}{\beta})\Gamma(\frac{2}{\beta})$, respectively [23]. The protocol for



Figure 5.1: Relative viscosity η_{rel} vs. concentration c in wt.% for aqueous suspensions of PNIPAM particles of different maximum swelling ratios α . The solid lines are fits to equation 2.14 of chapter 2.

estimating relaxation time, τ , of colloidal particles and the stretching exponent, β , using DLS is described in section 2.3.1 of chapter 2.

The thermoresponsive behavior of aqueous suspensions of PNIPAM particles is characterized in the temperature range 18 - 50°C at intervals of 2°C after allowing an equilibration time of 15 minutes for each temperature during cooling and heating. The maximum swelling ratio α of PNIPAM particles in aqueous suspensions is defined as $d_{20^{\circ}C}/d_{50^{\circ}C}$ ($d_{fullswell}/d_{fullshrunk}$), where $d_{20^{\circ}C}$ and $d_{50^{\circ}C}$ refer to the hydrodynamic diameters of the particles at 20°C and 50°C ($d_{fullswell}$ and $d_{fullshrunk}$) respectively. The maximum swelling ratios of PNIPAM particles synthesized at different SDS concentrations are listed in table 5.1.

The lower critical solution temperatures (LCSTs) of PNIPAM particles of different maximum swelling ratios in dense aqueous suspensions are estimated using differ-

α	<i>c</i> (<i>wt</i> .%)	$c_p(wt.\%)$	ϕ_{eff}
1.87	10.50	7.67	1.37
1.71	14.00	10.20	1.37
1.49	20.32	14.83	1.37

Table 5.2: Particle swelling ratios α , polymer concentration c, the fitted value of the polymer concentration, c_p , inside each particle in the swollen state, and the effective volume fraction ϕ_{eff} of the particles in aqueous suspension.



Figure 5.2: Heat flow as a function of temperature (T) for aqueous PNIPAM suspensions of different maximum swelling ratios (α) using DSC. The inset shows the plot of the LCST *vs.* the maximum swelling ratio α .

ential scanning calorimetry (DSC). The DSC setup is discussed in detail in section 2.7 of chapter 2. The heat flows estimated in the DSC experiments for aqueous PNIPAM suspensions of different maximum swelling ratios are plotted in figure 5.2 as a function of temperature T. The temperature corresponding to the endothermic peak in figure 5.2 is characterized as the LCST of the PNIPAM particles in aqueous suspensions. The values of LCSTs for PNIPAM particles of different maximum swelling ratios are shown in the inset of figure 5.2. It is seen that the LCSTs of PNIPAM particles in aqueous suspensions are approximately the same for all the maximum swelling ratios studied in this chapter.

The particle sizes at 25°C, maximum swelling ratios α , and polydispersity indices (PDIs) of aqueous PNIPAM suspensions measured from DLS experiments at an angle $\theta = 90^{\circ}$ are listed in table 5.1. The sizes of PNIPAM particles in aqueous suspensions are controlled by varying the SDS concentration in a free radical precipitation polymerization method. From the DLS data (table 5.1), it is observed that the sizes of PNIPAM particles in aqueous suspensions decrease with increase in SDS concentration. Particles of sizes 600 nm to 125 nm are synthesized by varying the SDS concentration from 0.01 g/L to 0.6 g/L.

Following the work of T. Hellweg *et al.* [24], we characterize the swelling property of PNIPAM particles by defining a temperature dependent swelling ratio, α . We measure the particle sizes as a function of temperature in temperature sweep DLS measurements. The thermoresponsive behavior of PNIPAM particles in aqueous suspensions is shown in figure 5.3(a). It is observed that PNIPAM particles in aqueous suspensions swell maximally below 20° C and shrink fully above 45° C. It is noted that the maximum swelling ratios, defined as $d_{20^{\circ}C}/d_{50^{\circ}C}$ $(d_{fullswell}/d_{fullshrunk})$, are 1.49 and 1.87 for the PNIPAM particles of sizes 600 nm and 125 nm that are prepared using 0.01 g/L and 0.6 g/L concentration of SDS respectively. Hence, the maximum swelling ratios of the PNIPAM particles in aqueous suspensions decrease with decrease in SDS concentration, which is accompanied by a simultaneous increase in particle size (table 5.1). The bigger PNIPAM particles in aqueous suspensions are therefore stiffer than the smaller particles. It is clear from the figure 1.9(b)of chapter 1 that PNIPAM particles are thermoreversible in aqueous suspensions, since the particle diameters remain the same regardless of whether the measurement is performed during the heating or the cooling cycle. In the experiments reported here, the effective volume fraction is kept constant in every experiment. Details of maximum swelling ratios used here, c and c_p and provided in table 5.2.

The size distributions of these particles measured from DLS data using the CON-TIN algorithm are shown in figure 5.3(b). The PDI values obtained from the DLS



Figure 5.3: (a) Temperature-dependent swelling ratios $d_{T^{\circ}C}/d_{50^{\circ}C}$ as a function of temperature *T* of aqueous PNIPAM suspensions for different concentrations of SDS. (b) Particle size distributions of PNIPAM particles measured from DLS experiments for different particle sizes synthesized using various SDS concentrations in the free radical polymerization method.

measurements for PNIPAM particles of different maximum swelling ratios are listed in table 5.1. A slight increase in the mean and width of the size distribution of PNIPAM particles in aqueous suspensions is observed with increase in particle size (figure 5.3(b)). Hence, from table 5.1 and figure 5.3(b), it is concluded that particles of low polydispersity indices can be synthesized by the one-pot free radical polymerization method. The results can be explained by considering that higher concentrations of SDS in the one-pot method results in the presence of a larger number of charged species on the surfaces of the primary particles at different nucleation times. This results in the stabilization of the particles in solution without further agglomeration, thereby resulting in smaller particles. The further growth of chains or the coalescence of the primary nuclei at lower SDS concentrations leads to the observed wider distribution of particle sizes.

The observed variation in maximum swelling ratios of the PNIPAM particles in aqueous suspensions (figure 5.3(a)) can be attributed to changes in the cross-linking density (CLD) of the particles. A higher CLD can enhance the stiffness of the

particles. The CLDs of the particles can be computed by estimating the Helmholtz free energies of the systems. The density of crosslinkers in microgels particles is much lower in comparison to that in polymers. The effect of crosslinks on the suspension can therefore be neglected and the Helmholtz free energy can be written as the sum of the free energies due to the stretching of the network $W_{stretch}$ and the mixing of the polymer and the solvent W_{mix} [25–27]:

$$W = W_{stretch}(\lambda_1, \lambda_2, \lambda_3) + W_{mix}(\alpha)$$
(5.1)

where λ_1 , λ_2 , λ_3 , the magnitudes of stretches in 3-dimensional cartesian coordinates for a rectangular block of gel in the swollen state, arise from the swelling of the particle below the LCST. Above the LCST, PNIPAM particles are essentially composed of the dry polymer network.

The stretching free energy is a function of the magnitudes of the stretches λ_1 , λ_2 , λ_3 , and depends on the crosslink density, while the free energy due to the mixing of the polymer and the solvent is a function of the maximum swelling ratio α . In an aqueous medium, the microgels absorb the solvent and swells freely. Assuming that the microgel swells by the same stretch in all directions, the expressions for the Helmholtz free energy of mixing and the Helmholtz free energy due to stretching of the network can be written as [28]

$$W_{mix} = \frac{k_B T}{\Omega} \left[(\alpha - 1) \log \left(1 - \frac{1}{\alpha} \right) + \chi \left(1 - \frac{1}{\alpha} \right) \right]$$
(5.2)

$$W_{stretch} = \frac{1}{2} N k_B T \Big[3\alpha^{2/3} - 3 - 2\log\alpha \Big]$$
(5.3)

where Ω is the volume per water molecule, N is the number density of the crosslinks which is the number of crosslinkers divided by the volume of the dry polymer and χ , the dimensionless measure of the strength of the pairwise interactions between the species, is a function of temperature, T, and volume fraction of the polymer in the microgel, ϕ .



Figure 5.4: Average hydrodynamic diameter $\langle d_H \rangle$ of the PNIPAM particles in aqueous suspensions at 20°C as a function of maximum swelling ratio α . The solid line is a fit to equation 5.7.

The Helmholtz free energy of the freely swelling microgel particles is finally written as the sum of the W_{mix} and $W_{stretch}$ as a function of χ , α and N.

$$W(\alpha, T) = \frac{1}{2} N k_B T \Big[3\alpha^{2/3} - 3 - 2\log\alpha \Big] + \frac{k_B T}{\Omega} \Big[(\alpha - 1)\log\left(1 - \frac{1}{\alpha}\right) + \chi \Big(1 - \frac{1}{\alpha}\Big) \Big] \quad (5.4)$$

At a particular temperature, the free energy will have a minimum, corresponding to the stable state (swollen or shrunken state) at equilibrium. Hence the first order derivative of the free energy W with respect to the maximum swelling ratio α should vanish:

$$\frac{\partial W(\alpha, T)}{\partial \alpha} = Nk_B T \Big[(\alpha^{-1/3} - \alpha^{-1}) + \frac{1}{N\Omega} \Big(\log \Big(1 - \alpha^{-1} \Big) + \alpha^{-1} + \chi \alpha^{-2} \Big) \Big] = 0$$
(5.5)

S DS	$d_{20^{\circ}C}$	α	N
$0.01 \ g/L$	613 nm	1.49	$2.60 \times 10^{19} m^{-3}$
$0.06 \ g/L$	457 nm	1.63	$1.94 \times 10^{19} m^{-3}$
$0.15 \ g/L$	274 nm	1.71	$1.66 \times 10^{19} m^{-3}$
0.3 g/L	161 nm	1.80	$6.83 \times 10^{18} m^{-3}$
$0.6 \ g/L$	131 <i>nm</i>	1.87	$5.56 \times 10^{18} m^{-3}$

Chapter 5. Influence of particle size on the thermoresponsive and rheological properties of aqueous poly(N-isopropylacrylamide) colloidal suspensions

Table 5.3: Calculated crosslink density N per particle from the fitting parameters d_{α_0} and χ for different sizes of the particles synthesized by varying the SDS concentration in the free radical precipitation polymerization method. $d_{20^\circ C}$ and α are the hydrodynamic diameters at 20°C and maximum swelling ratios of PNIPAM particles in aqueous suspensions, respectively.

Equation 5.5 results in a useful relation between the crosslink density N and the maximum swelling ratio α .

$$N\Omega = \frac{\log(1 - \alpha^{-1}) + \alpha^{-1} + \chi \alpha^{-2}}{\alpha^{-1} - \alpha^{-1/3}}$$
(5.6)

The swelling of the PNIPAM particles is a measure of the crosslink density and increases with reaction time [18]. This gives rise to a linear relation between the crosslinking density and the average hydrodynamic diameter of the PNIPAM particles: $N = k < d_H^T >$. Using this relation in equation 5.6, we get

$$< d_H^T >= d_{\alpha_0} \Big[\frac{\log(1 - \alpha^{-1}) + \alpha^{-1} + \chi \alpha^{-2}}{\alpha^{-1} - \alpha^{-1/3}} \Big]$$
 (5.7)

where k is the proportionality constant establishing a relation between the crosslinking density of a particle with its size, $\langle d_H^T \rangle$ is the diameter of the particle at a temperature T and $d_{\alpha_0} = 1/k\Omega$.

The mean hydrodynamic diameter $\langle d_H \rangle$ at 20°C vs. the maximum swelling ratio α is plotted in figure 5.4. The solid line is a fit of the data to equation 5.7. The values of the fitting parameters d_{α_0} and χ , obtained from fitting the data are 784 ± 294 nm and 0.60 ± 0.11 respectively. The value of d_{α_0} can be used to calculate the CLD per particle. The CLDs for different particle sizes at 20°C are calculated using the relation: $N = d_T/d_{\alpha_0}\Omega$ and are shown in table 5.3. From this table, it is clear that bigger particles have higher CLDs and hence are stiffer. This is because the higher SDS concentration stabilizes the primary particles at the early stage of nucleation, thereby resulting in smaller particles and a lower crosslinker density inside the particle. However, if the SDS concentration is low, a longer time is required to stabilize the particles, due to which we get larger sizes and higher crosslinker concentrations inside the particles.

The PNIPAM particles in dry state are visualized using a scanning electron microscope (SEM, GEMINI column, ZEISS, Germany with an accelerating of 5 kV). The details of the procedure are given in section 2.6 of chapter 2. The SEM images of aqueous PNIPAM suspensions for different maximum swelling ratios are shown in figure 5.5 (a-e). The average sizes $< d_H >$ of the PNIPAM particles, at 25 °C, estimated from SEM images, are plotted in figure 5.5(f) vs. the maximum swelling ratio α . The error bars correspond to the standard deviation of the particle sizes. It is seen that the particle size increases with decrease in the maximum swelling ratio α (figure 5.5(f)). A slight increase in the width of the distribution of the particle size is observed with decrease in α . This observation agrees well with the DLS results reported earlier in this chapter. However, the sizes of the particles estimated from SEM images are found to be less than those measured from DLS experiments at 50°C. This is because at temperature above the LCST (50°C), the PNIPAM particles in suspension shrink by expelling water, but are still not collapsed fully. The particles visualized in the SEM images are, on the other hand, in the completely dry state. The DLS experiments therefore produce larger values of $< d_H >$ compared to the SEM images in which the particles are in a dried state.

Temperature sweep experiments at a fixed oscillatory strain amplitude 0.3% and angular frequency 1rad/s are performed to study the temperature dependence of



Figure 5.5: SEM images of PNIPAM particles at 25°C, synthesized by free radical polymerization method with different concentrations of SDS: (a) 0.6 g/L, (b) 0.3 g/L, (c) 0.15 g/L, (d) 0.06 g/L, and (e) 0.01 g/L. The scale bar corresponds to a length of 200 nm. (f) The average diameter of PNIPAM particles in aqueous suspensions estimated from SEM images as a function of maximum swelling ratios α .

the viscoelastic moduli G' and G''. The temperature is changed at the rate of 1°C/min in both cooling and heating experiments. The temperature responses of the viscoelastic moduli G' and G'' for aqueous PNIPAM suspensions of three different maximum swelling ratios 1.87, 1.71, and 1.49 at an effective volume fraction $\phi_{eff} =$ 1.37 are shown in figure 5.6(a). It is clear from the inset of figure 5.6(a) that for the same effective volume fraction $\phi_{eff} =$ 1.37 below the LCST ($T = 20^{\circ}$ C), the elastic



Figure 5.6: (a) Elastic modulus G' (solid symbols) and viscous modulus G'' (open symbols) of aqueous PNIPAM suspensions of different maximum swelling ratios as a function of temperature T. (b) The difference between the elastic modulus and the viscous modulus, G' - G'', vs. temperature T for aqueous suspensions of PNIPAM particles of different maximum swelling ratios α . (c) Plot of the LCST, estimated from the rheological measurements, as a function of maximum swelling ratios α .

modulus G' of the suspensions increases with decrease in maximum swelling ratio. It is observed that below the LCST, the elastic modulus G' dominates over the viscous modulus G'', which indicates that the system is a viscoelastic solid under these conditions. As the temperature increases, both G' and G'' decrease. The difference between the two moduli G' - G'', which is a measure of the relative rigidity of the viscoelastic suspension, is plotted in figure 5.6(b). It is noted that the relative rigidity gets smaller as the temperature increases and eventually becomes negligible near the LCST. This indicates that the system loses its rigidity near the LCST. For the soft particles ($\phi_{eff} = 1.87$), the viscous modulus G'' dominates over the elastic modulus G' near the LCST which indicates liquid like behavior of the system. This can be attributed to the sudden collapse in the sizes of PNIPAM particles near the LCST. The temperature at which both G' and G'' abruptly decrease is characterized as the LCST of the aqueous PNIPAM suspension. As the temperature



Figure 5.7: ((a) The temperature dependent storage modulus G' and loss modulus G'' while heating and cooling a suspension of PNIPAM particles of swelling ratio = 1.87. (b) The temperature dependent storage modulus G' and loss modulus G'' while heating and cooling a suspension of PNIPAM particles of swelling ratio = 1.49.

is increased beyond the LCST, a gradual increase in the moduli is observed. The above result agrees well with the observations reported in an earlier work [13]. It has been reported that the interaction between the PNIPAM particles in aqueous suspensions changes from repulsive to attractive at the LCST. The increase in both the moduli at temperatures above the LCST is attributed to an increase in the attractive interactions between the PNIPAM particles in aqueous suspensions. This leads to the formation of gel networks which manifests as an increase in the moduli at these temperatures. The LCST of the PNIPAM particles of different maximum swelling ratios in aqueous suspensions, estimated from the rheological measurements, are plotted figure 5.6(c). We note that the LCST values of PNIPAM particles in aqueous suspensions measured from temperature sweep rheology experiments match closely with the LCST values estimated from the DSC measurements (inset of figure 5.2).

Figure 5.7(a-b) show the temperature dependence of G' and G'' while heating and cooling for PNIPAM particles in aqueous suspensions having maximum swelling ratios 1.87 and 1.49 respectively. It is observed that both the viscoelastic moduli G'and G'' follow the same paths during both cooling and heating cycles for suspensions

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of the stiffer PNIPAM particles of swelling ratio 1.49 (figure 5.7(b)). However, the viscoelastic moduli for suspensions of the soft particles ($\phi_{eff} = 1.87$) are observed to deviate from each other near the LCST while cooling (figure 5.7(a)). The observed behavior of G' and G'' for the soft PNIPAM particles in aqueous suspensions can be attributed to changes in the particle packing behavior due to their higher thermoresponsivity and deformability.

5.4 Conclusions

Thermoresponsive PNIPAM particles of different sizes are synthesized by varying the SDS concentration in the free radical precipitation polymerization method. Increasing the concentration of SDS produces smaller and relatively softer particles having lower polydispersity indices. The stiffnesses of the particles are quantified in terms of their maximum swelling ratios. This chapter estimates the variation of the maximum swelling ratios of the particles with their sizes and demonstrates that changes in the stiffness of the particles with changing size can be attributed to the different crosslink densities (CLDs) of the particles. The CLDs of PNIPAM particles in aqueous suspensions, estimated using a statistical model for the Helmholtz free energies of the microgel and written as a function of the particle maximum swelling ratio α , is observed to increase with decrease in maximum swelling ratio. The viscoelastic moduli of these particles in aqueous suspensions at an effective volume fraction $\phi_{eff} = 1.37$, measured from temperature sweep experiments, are observed to increase with decrease in swelling ratios at a temperature below the LCST (at 20°C). Decrease in both moduli is observed with increase in temperature. The temperature at which both G' and G'' show a minimum value is characterized as the LCST of the particles in the aqueous suspension. The LCST values of PNIPAM particles in aqueous suspensions, measured using differential scanning calorimetry, closely match those obtained in rheological measurements.

Particle packing studies are important to understand the dependence of the colloidal glass transition on particle parameters such as their sizes, size distributions, stiffnesses, and their packing configurations [10, 16, 29–31]. Since the properties of PNIPAM particles in aqueous suspensions can be controlled by tuning the temperature of the medium and the stiffnesses of the constituent particles, PNIPAM suspensions can potentially be used as multifunctional materials [32]. The formation of aggregates by PNIPAM particles in aqueous suspensions above the LCST can be used to study the onset of film formation [33, 34]. The swelling and deswelling properties of aqueous PNIPAM suspensions can be exploited in sensor devices [8, 35]. Research involving the controlled synthesis and aggregation mechanism of PNIPAM particles in aqueous suspensions is therefore very important.

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Chapter 6

Role of microgel stiffness in particle self-assembly and suspension rheology across the lower critical solution temperature

6.1 Introduction

Colloidal suspensions have been studied extensively and systematically because of their importance in modeling phenomena such as the glass transition [1–5], and for their applicability in therapeutics and in the manufacture of food, paints, sensors etc [3, 6–11]. Soft deformable colloidal particles, which can be produced by crosslinking polymer particles immersed in a solvent, offer an advantage over many hard colloidal particles due to their significant swelling and deswelling properties in response to changes in external stimuli such as temperature, pH and solvent composition [6, 12–14].

In recent years, researchers have comprehensively investigated the complex phase behavior, temperature or volume fraction induced interparticle interactions and jamming dynamics of dense suspensions of soft thermoresponsive poly(N-isopropylac-rylamide) (PNIPAM) colloidal microgel particles [6, 15–19]. Thermoresponsive behavior of PNIPAM microgel particles in aqueous suspensions are discussed in detail in section 1.6 of chapter 1. Their thermoreversible nature makes PNIPAM suspensions ideal candidates for drug delivery and in the preparation of strong gels in the design of soft biomimetic devices [9, 20]. Nanocomposite PNIPAM microgels have been shown to exhibit highly robust mechanical properties. For instance, it has been demonstrated recently that poly(acrylamide) nanocomposite microgels can resist compressive and tensile stresses of the order of megapascals [21]. The excellent

mechanical resilience and thermoresponsivity of microgel suspensions make them suitable for use as multifunctional materials in biomedical engineering [20, 22].

Recent research has established the length-scale dependent rheology of PNIPAM suspensions [23]. Using rheo-dielectric technique, the authors of this study reported that the PNIPAM particles exhibit distinct dynamics at very different length scales (7-8 orders of magnitudes) under applied shear. In the present work, we investigate the mechanical properties, self-assembled microstructures and phase transformations of dense PNIPAM suspensions while controlling the medium temperature and stiffnesses of individual particles. It has been demonstrated experimentally that PNIPAM particle stiffness can be altered by varying the concentration of the crosslinker (N, N'-methylenebisacrylamide) while keeping the concentrations of the monomer (N-isopropylacrylamide) and the surfactant (sodium dodecyl sulfate -SDS) fixed during the synthesis process [24–26]. The dependence of suspension rheology on particle stiffness was recently tested experimentally for dense suspensions of PNI-PAM particles crosslinked with glutaraldehyde [27]. The authors of this study used a schematic mode coupling theory (MCT) to model the linear rheology of the samples below the LCST. According to another study, a suspension of relatively stiff ionic microgel particles below its LCST shows a transition from liquid to crystal to glass with increase in volume fraction [16]. In contrast, suspensions of particles of intermediate stiffnesses transform from liquid to glass without going through an intermediate crystal phase. Interestingly, suspensions of the softest particles always remained liquid-like across the range of volume fractions explored in the study. Iyer *et al.* [28] studied the self healing properties of microgel colloidal crystals in the presence of particle-size irregularity and reported that the self-assemblies of these particles are defect tolerant due to the deformability and compressibility of the constituent particles. They reported that microgels exhibit characteristics of both polymeric and colloidal systems. It has been reported that the rheological properties of PNIPAM suspensions depend on the synthesis protocol, average particle size, size polydispersity and particle crosslinking density [3, 25, 26]. A higher crosslinking density leads to a higher interparticle force, thereby increasing the plateau value of the elastic modulus [25]. In contrast, the easy penetration of the long dangling polymer chains present on the surfaces of particles with lower crosslinking densities results in higher yield stresses.

The temperature-dependent phase behavior of dense aqueous PNIPAM suspensions has been widely studied in the literature [2, 6, 7]. Using dynamic light scattering and rheological measurements, J. Mattsson *et al.* [2] studied the glass transition dynamics of dense suspensions of microgels comprising interpenetrated networks of PNIPAM and PAAc (polyacrylic acid). They reported that these suspensions mimic molecular glass formers, with suspension fragility decreasing with decreasing microgel stiffness. Romeo *et al.* have reported that the glassy state formed by temperature- and pH-responsive PNIPAM suspensions at low temperature liquefies at the LCST before solidifying into a gel-like state at higher temperaturedependent changes in the Flory-Huggins parameter, with the suspension existing in a repulsive glass phase below the LCST and transforming to a percolating attractive gel phase above the LCST [6, 29]. While stiffness and temperature-induced phase changes in PNIPAM suspensions have been investigated separately, a systematic study of the effects of microgel stiffness on particle self-assembly, phase behavior and dense suspension rheology over a wide temperature range is absent in the literature to the best of our knowledge.

In this chapter, we synthesize PNIPAM particles of different stiffnesses by varying the concentration of the crosslinker in a free radical precipitation polymerization synthesis method. The particles are then suspended in an aqueous medium to form dense suspensions. Mechanical properties of these suspensions, such as their linear viscoelastic moduli and yield stresses, are studied in oscillatory rheology experiments. Particle stiffness is quantified in terms of a maximum swelling ratio. We report that for a fixed volume fraction below the LCST, the elasticity of a dense aqueous PNIPAM suspension increases with increase in particle stiffness. The viscoelastic moduli of the suspension are seen to decrease by orders of magnitude at the LCST $\approx 34^{\circ}$ C and then display a steady increase when suspension temperature is increased above the LCST. This confirms the results of the study by Romeo etal. [6]. We systematically analyze the observed results in terms of changes in PNI-PAM particle hydrophobicity which we estimate using Fourier transform infrared (FTIR) spectroscopy. Finally, we correlate the macroscopic mechanical behavior (bulk rheology) of these dense suspensions to their microscopic structures by directly visualizing the cryo-frozen samples using a cryogenic scanning electron microscope (cryo-SEM). Cryo-SEM images of dense suspensions of soft PNIPAM particles, prepared at temperatures below and above the LCST, show that the underlying suspension structures are constituted by honey-comb like networks. For suspensions prepared at the LCST, we note the coexistence of liquid-like and highly porous gellike phases. Suspensions of stiff particles, in contrast, always assemble in a glassy state over the entire temperature range. Our study reveals that the temperaturedependent phase behavior of dense PNIPAM suspensions can be effectively tailored by controlling the degree of crosslinking and therefore the stiffnesses of the constituent particles. We believe that a clearer understanding of these suspensions will

NIPAM	MBA	KPS	S DS	α	c_p	ϕ_{eff}	С
(g)	(% of NIPAM)	(g)	(g)	$(d_{fullswell}/d_{fullshrunk})$	(wt.%)		(wt.%)
7	1.0	0.28	0.03	≈3.36	3.63	1.5	5.44
7	2.5	0.28	0.03	≈2.56	5.06	1.5	7.59
7	5.0	0.28	0.03	≈2.00	7.57	1.5	11.35
7	10.0	0.28	0.03	≈1.66	10.87	1.5	16.30
7	15.0	0.28	0.03	≈1.51	17.00	1.5	25.5
7	20.0	0.28	0.03	≈1.41	21.63	1.5	32.44
7	25.0	0.28	0.03	≈1.33	28.82	1.5	43.23

Table 6.1: Synthesis conditions used for the preparation of PNIPAM particles by the onepot polymerization method and characterization of the swelling properties (stiffnesses) of the synthesized particles. PNIPAM particles were prepared in 500 mL volume. α , c_p , ϕ_{eff} , c are the maximum swelling ratio, polymer concentration inside each PNIPAM particle, effective volume fraction and particle concentration in aqueous suspension at temperature 25° C, respectively.

trigger further research on their utility as multifunctional materials [20].

6.2 Sample preparation and experimental methods

Poly(*N*-isopropylacrylamide) (PNIPAM) particles of different stiffnesses were synthesized by varying the crosslinker concentration (*N*, *N'*-methylenebisacrylamide (M-BA)) in a free radical precipitation polymerization process. The details of the synthesis procedure is described in section 2.2.2 of chapter 2. After particle synthesis, fine powder was prepared by grinding the dried particles using a mortar and pestle. The synthesis conditions and the swelling properties of the synthesized particles are tabulated in table 6.1. Dense aqueous PNIPAM suspensions were prepared by adding PNIPAM powder in Milli-Q water. The samples were stirred for 24 hours and sonicated for 15 minutes. The dense suspension was diluted to prepare PNI-PAM suspensions of other concentrations. Since PNIPAM particles are deformable, volume fraction ϕ is not an appropriate measure to quantify their packing in aqueous suspensions. Therefore, a modified parameter called effective volume fraction, ϕ_{eff} ,



Figure 6.1: (a) Relative viscosity η_{rel} vs. particle concentration c in wt.% for aqueous suspensions of PNIPAM particles synthesized with different crosslinker concentrations at a temperature 25°C. The solid lines are fits to the Cross model (equation 2.13 of chapter 2).

is used. Figure 6.1 shows the plot of relative viscosity as a function of particle concentration for aqueous suspensions of PNIPAM particles synthesized using different concentrations of MBA. The protocol for estimating the effective volume fractions of PNIPAM particles in suspension using figure 6.1 is discussed in detail in section 2.4.1a(i) of the chapter 2. Concentrations of ingredients were chosen here to ensure an effective volume fraction $\phi_{eff} = 1.5$ at $T = 25^{\circ}$ C. The experimental techniques used in this chapter (DLS, rheology, DSC and cryo-SEM) are discussed in detail in chapter 2.

6.3 Results and discussions

Dynamic light scattering (DLS) experiments were performed to quantify the average sizes and thermoresponsive behaviors of PNIPAM particles of different stiffnesses in dilute suspensions. The details of the DLS setup and protocols for estimating sizes of colloidal particles are discussed in section 2.3 of chapter 2. Very dilute suspensions $(\phi_{eff} \approx 10^{-4})$ were prepared by adding dried PNIPAM powder in Milli-Q water. A glass cuvette, filled with 5.0 mL of the suspension, was placed in the sample holder of the DLS setup. We measured the hydrodynamic sizes $\langle d_H \rangle$ of the thermoresponsive PNIPAM particles within a temperature range between 16°C and 55°C at intervals of 2°C. We quantified the swelling behavior of PNIPAM particles by measuring their maximum swelling ratios, α , defined as $d_{20^\circ C}/d_{45^\circ C}$, where $d_{20^\circ C}$ and $d_{45^\circ C}$ refer to the average hydrodynamic diameters of the particles at 20°C and 45°C where they are fully swollen and fully shrunken/ collapsed respectively.

Figure 6.2 shows the temperature-dependent swelling ratios, $\alpha_T = d_{T^\circ C}/d_{45^\circ C}$, where d_T is the average hydrodynamic diameter of the particles at temperature T. Due to their higher osmotic pressure, the polymer networks in PNIPAM particles with low crosslinker concentration undergo rapid expansion upon incorporating water [25, 30]. We see from figure 6.2 that the volume phase transition of these particles at the LCST becomes more continuous with increase in crosslinker concentration. We were able to synthesize PNIPAM particles with maximum swelling ratios α ranging from 3.36 (soft particles) to 1.33 (stiff particles) by varying crosslinker concentrations from 1.0 to 25.0 % of the NIPAM monomer mass. The values of α corresponding to the various concentrations of the crosslinker MBA are listed in table 6.1 and are plotted in the inset of figure 6.2. We see from the inset of figure 6.2 that with increase in crosslinker (MBA) concentration, the maximum swelling ratios, α , of PNIPAM particles in aqueous suspension decrease, signaling an increase in the stiffnesses of these particles. In this chapter, we have designated PNIPAM



Figure 6.2: Temperature-dependent swelling ratios, $\alpha_T = d_{T^\circ C}/d_{45^\circ C}$, where $d_{T^\circ C}$ and $d_{45^\circ C}$ are the average hydrodynamic diameters of PNIPAM particles at temperatures T and $45^\circ C$ respectively, synthesized with different crosslinker concentrations in dilute aqueous suspensions. The inset shows the dependence of maximum swelling ratios α of these particles on the concentration of the crosslinker used during particle synthesis.

particles with maximum swelling ratios $\alpha \ge 2.56$ as soft particles, particles with 1.51 $\le \alpha \le 2$ as those of intermediate stiffnesses and particles with swelling ratios < 1.51 as stiff particles.

FTIR spectra were measured using Shimadzu IR Tracer-100 Fourier Transform Infrared Spectrophotometer. A 0.3wt.% PNIPAM suspension prepared in D₂O was loaded in a sample cell sandwiched between two zinc sulfide (ZnS) plates separated using a teflon spacer of thickness 1 mm. The temperature of the sample cell was controlled using a water circulation unit (Julabo 300F). D₂O was used instead of H₂O to avoid overlap of the amide I band of PNIPAM (associated with C=O stretching) with the O-H bending mode of water [31, 32]. FTIR absorption data at different



Figure 6.3: FTIR absorption spectra of suspensions of PNIPAM particles (0.3wt.% prepared in D₂O) synthesized with different crosslinker concentrations: (a) 1 % ($\alpha = 3.36$), (b) 5% ($\alpha = 2.00$) and (c) 25% ($\alpha = 1.33$) of NIPAM monomer mass at different suspension temperatures.

temperatures are plotted in figures 6.3(a)-(c) for PNIPAM particles of three different stiffnesses. We observe two absorption peaks centered around wavelengths 1625cm⁻¹ and 1460cm^{-1} (with peak heights designated as A₂ and A₁ respectively in figure 6.4), which are respectively associated with amide I (C=O stretching and H-bonding interactions) and amide II (N-H bending and C-N stretching vibrations) modes in PNIPAM [31, 32]. With increase in temperature, the decrease in height of the absorption peak at 1625cm^{-1} (A₂(1625) in figure 6.4(a)) reveals the dehydration or increase in hydrophobicity of PNIPAM particles [31, 32]. It can be clearly seen from figure 6.4(a) that the absorption peak height of the amide I mode increases with increase in the stiffness of PNIPAM particles, thereby clearly indicating a monotonic increase in hydrophilicity with increase in particle stiffness. This is attributed to the presence of larger crosslinker (N, N'-methylenebisacrylamide) concentrations of the polar groups, N-H and C=O<, in stiff PNIPAM particles [33, 34]. The increase in absorption peak height of the amide II mode $(1460 \text{cm}^{-1} \text{ in figure } 6.4(b))$ with increase in temperature confirms the formation of intra- or interchain hydrogen bonds between N-H and C=O<[31, 32] and agrees with our earlier observation that PNIPAM particle hydrophobicity increases with temperature and decreases with increasing particle stiffness.



Figure 6.4: (a) Absorption peak heights, centered at 1625cm^{-1} (obtained from FTIR spectra) vs. temperature T for suspensions constituted by PNIPAM particles of different stiffnesses, characterized by maximum swelling ratios α . (b) Absorption peak heights, centered at 1460cm^{-1} as a function of T for PNIPAM particles of the same stiffnesses in suspension. The spectra are displayed in figures 6.3(a-c).

We have estimated the temperature-dependent ϕ_{eff} using the relation $\phi_{eff}(T) = \phi_{eff}(25^{\circ}C) \times (\frac{d_h(T)}{d_h(25^{\circ}C)})^3$ [35], where $\phi_{eff}(T)$, $\phi_{eff}(25^{\circ}C)$, $d_h(T)$ and $d_h(25^{\circ}C)$ are ϕ_{eff} at temperatures T and $25^{\circ}C$ and average hydrodynamic diameters of PNIPAM par-



Figure 6.5: Temperature-dependent ϕ_{eff} of aqueous suspensions of PNIPAM particles of different maximum swelling ratios, α . The vertical purple line represents the estimated effective volume fraction of 1.5 at 25°C. The arrow points towards the direction of increase in particle stiffness, which coincides with the direction of decrease in maximum swelling ratio, α . Inset shows effective volume fractions of the suspensions at temperatures 55°C (above LCST) and 25°C (below LCST). While the suspensions all have $\phi_{eff} = 1.5$ below the LCST, ϕ_{eff} varies inversely with α above the LCST because of the different deswelling rates of particles of different α .

ticles at T and 25°C, respectively. The temperature-dependent $\phi_{eff}(T)$ of aqueous suspensions of PNIPAM particles ($\phi_{eff} = 1.5$ at 25°C) synthesized with different crosslinker concentrations are plotted in figure 6.5. Since soft particles deswell more than stiff particles, we note from the inset of figure 6.5 that the effective volume fraction, ϕ_{eff} , decreases rapidly with increase in maximum swelling ratio α above the LCST, even though ϕ_{eff} was same for all the suspensions at 25°C (i.e., below the LCST).



Figure 6.6: Heat flow as a function of temperature T for aqueous suspensions of PNIPAM particles of different maximum swelling ratios α . (b) Plot of LCST values of PNIPAM particles in dense aqueous suspensions vs. maximum swelling ratio, α .

The heat flows evaluated in the differential scanning calorimetry (DSC) experiments (details of the DSC measurements are discussed in section 2.7 of chapter 2) for aqueous suspensions of PNIPAM particles of different α are plotted in figure 6.6(a) as a function of temperature T. The temperatures corresponding to the endothermic peaks are characterized as the LCSTs of the PNIPAM particles in aqueous suspension. Figure 6.6(b) shows the LCST values of suspensions of PNIPAM particles of different α . We note a slight decrease in the LCST of PNIPAM particles with increase in α . The stiffer particles are more hydrophilic than the softer particles due to the presence of a larger number of polar groups (N-H and C=O) resulting from the higher concentrations of the crosslinker (N, N'-methylbisacrylamide) used during their synthesis. The LCSTs of suspensions of stiffer particles are therefore higher.

6.3.1 Temperature dependent swelling and mechanical properties of PNIPAM suspensions

We have systematically studied the temperature-dependence of the self-assembled structures, rheology and phase behavior of dense aqueous suspensions of PNIPAM

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Figure 6.7: (a) Temperature dependent elastic moduli G' (solid symbols) and viscous moduli G'' (hollow symbols), of aqueous suspensions of PNIPAM particles of different stiffnesses (or swelling ratios α), prepared at identical effective volume fraction, $\phi_{eff} = 1.5$, at 25°C. (b) The measure of suspension relative rigidity, G' - G'', vs. temperature T, for aqueous suspensions of PNIPAM particles of different maximum swelling ratios α . (c) LCST values of PNIPAM particles in dense aqueous suspensions, estimated from rheological measurements (red symbols) and DSC experiments (blue symbols) vs. α .

particles of different stiffnesses. To study the temperature-dependent mechanical properties of these suspensions, we perform temperature sweep rheological experiments at a fixed oscillatory strain amplitude 0.5% and angular frequency 0.5 rads^{-1} . Figure 6.7(a) shows a plot of the elastic and viscous moduli, G' and G'', as a function of temperature T for aqueous suspensions of PNIPAM particles of different stiffnesses, having effective volume fraction, $\phi_{eff} = 1.5$ at 25°C. Below the LCST, we observe that both G' and G'' increase with increase in particle stiffness. This is in agreement with previous work that reported increase in suspension elasticity with increase in particle crosslinker density [7]. According to Mattsson *et al.* [2], the fragility of a colloidal glass is determined by particle-scale elasticity. Since stiff particles swell less than soft particles in aqueous suspension, we have used a larger concentration of the former to achieve the same effective volume fraction at 25°C (table 6.1). Increase in particle number density and bulk modulus of individual PNI-PAM particles explain the larger G' of suspensions of stiffer particles. For all the samples, the elastic modulus, G', exceeds the viscous modulus, G'', at T < LCST, indicating viscoelastic solid-like behavior at these temperatures due to the jamming of the swollen PNIPAM particles. We also note a collapse of the moduli at the LCST due to a sharp reduction in the swelling ratios of the constituent particles (figures 6.7(a-b)). The more rapid collapse in the viscoelastic moduli of suspensions of soft PNIPAM particles at the LCST can be attributed to their rapid deswelling. Both viscoelastic moduli are minimum at their LCSTs. We see from figure 6.7(c)that the LCSTs estimated from the rheology and DSC data show excellent overlap. On raising the temperature beyond the LCST, we observe a gradual increase in the viscoelastic moduli, with G' eventually exceeding G'' for all the suspensions. Figure 6.7(b) displays plots of G' - G'', which is a measure of the relative rigidity of the viscoelastic suspensions, over the range of temperatures explored here. For all the suspensions, we observe a significant loss of rigidity near the LCST. Interestingly, we note that G'' > G' near the LCST for only the suspension of the softest PNI-PAM particles ($\alpha = 3.36$, indicated by the olive circle in figure 6.7(b)), revealing viscoelastic liquid-like behavior. Using suspensions of PNIPAM particles of a fixed swelling ratio, Romeo *et al* [6] had reported a transformation from a repulsive glass to an attractive gel phase, while passing through a liquid-like state near the LCST, due to temperature-dependent changes in the Flory-Huggins parameter. The increase in suspension rigidity at temperatures above the LCST can be attributed to an increase in the attractive interactions between the increasingly hydrophobic PNIPAM particles in aqueous suspension. Interestingly, we observe that aqueous suspensions of stiff particles do not exhibit a liquid phase near the LCST. This can be attributed to the higher number density of stiffer particles used during suspension preparation (table 6.1). We see, therefore, that the solid-solid transition of dense aqueous suspensions of PNIPAM particles across the LCST depends on the stiffness of the constituent particles.

6.3.2 Influence of underlying suspension microstructures on macroscopic mechanical properties

6.3.2a Frequency sweep rheology to explore linear rheological properties

We next perform frequency sweep rheological experiments at a fixed strain amplitude, $\gamma = 0.5\%$, to study the dynamics of dense aqueous suspensions of PNIPAM particles of different stiffnesses at temperatures below, near and above the LCST. Our frequency sweep data reveal enhanced mechanical properties of the suspensions with increase in particle stiffness. This is in agreement with the temperature sweep rheological data plotted in figure 6.7(a). Below LCST, the PNIPAM suspensions display approximately frequency independent G' and weakly frequency dependent G'' values (figures 6.8(a,d,g)), indicating the existence of slow glassy dynamics in these samples. For the suspension constituted by the softest PNIPAM particles ($\alpha = 3.36$, figure 6.8(a)), we observe the existence of two crossover points in the high and low frequency regimes, presumably arising from two different relaxation mechanisms. Crossover points for other samples, arising from changes in relax-



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Figure 6.8: Elastic moduli, G' (solid symbols), and viscous moduli, G'' (hollow symbols), as a function of applied oscillatory frequency, ω , for aqueous suspensions of (a-c) soft PNI-PAM particles, (d-f) PNIPAM particles of intermediate stiffnesses and (g-i) stiff PNIPAM particles, at temperatures below the LCST, near the LCST and above the LCST, prepared at $\phi_{eff} = 1.5$ at 25°C.

ation rates, are expected to occur outside the frequency window explored in this study. The noisy frequency sweep data for aqueous suspensions of soft PNIPAM particles at a temperature near the LCST (figure 6.8(b)) indicates its liquid-like nature. In contrast, the frequency-dependent viscoelastic behavior of suspensions of PNIPAM particles of intermediate and large stiffnesses at the LCST (figures 6.8(e) and 6.8(h) respectively) indicates the presence of weak gels/ glasses. Above the LCST, the observed increase in G' with frequency, together with a minimum in G'' at a characteristic frequency (figure 6.8), are typical characteristics of glasses or gels composed of hard attractive colloids [36–38]. This observation indicates the forma-



Figure 6.9: Elastic moduli, G' (solid symbols), and viscous moduli, G'' (hollow symbols), as a function of applied strain amplitude, γ , for aqueous suspensions of (a-c) soft PNIPAM particles, (d-f) PNIPAM particles of intermediate stiffnesses and (g-i) stiff PNIPAM particles, at temperatures below the LCST, near the LCST and above the LCST, prepared at $\phi_{eff} = 1.5$ at 25°C.

tion of phases driven by attractive hydrophobic interactions between the collapsed PNIPAM particles. We note that the mechanical moduli of the suspensions comprising soft particles are considerably lower above the LCST than below it. Moduli characterizing suspensions of the stiffer particles, in contrast, are comparable below and above the LCST.

6.3.2b Amplitude sweep rheology to explore yielding properties

We perform oscillatory strain amplitude sweep rheological experiments at a fixed angular frequency $\omega = 0.5 \text{rads}^{-1}$ to study the non-linear viscoelastic properties of



Figure 6.10: (a) Linear modulus, G'_l , vs. temperature T for aqueous PNIPAM suspensions characterized by different stiffnesses. (b) Yield stresses, σ_y , as a function of T for aqueous PNIPAM particle suspensions with the same particle stiffnesses.

dense aqueous suspensions of PNIPAM particles of different stiffnesses and at various suspension temperatures. Figure 6.9 displays strain amplitude sweep data for all the samples. Apart from the suspension of the softest particles at the LCST (figure 6.9(b)) which exhibits liquid-like rheology, we note that both elastic and viscous moduli, G' and G'', of the other samples are independent of the applied strain amplitude for small strain amplitudes, while G' > G'', indicating viscoelastic solid-like behavior. With increase in applied strain amplitude, the suspensions start yielding, as indicated by a monotonic decrease in the elastic modulus, G', at higher strains. Simultaneously, the viscous modulus, G'', shows a peak before decreasing,



Figure 6.11: Viscoelastic moduli, G' and G'' (represented by solid and open circles respectively), and elastic stresses, σ_{el} (solid squares), vs. strain, γ , for suspensions of PNIPAM particles of maximum swelling ratio $\alpha = 1.66$ at (a) 15°C (below LCST) and (b) 55°C (above LCST). The solid line is a linear fit to the σ_{el} vs. γ data. (a) The horizontal and vertical dashed lines represent yield stress, σ_y , and yield strain, γ_y , respectively. (b) The first and second yield stresses (σ_{y1} and σ_{y2}) are shown by horizontal green and black dashed lines respectively.

which signals the onset of an yielding process. G'' eventually exceeds G', at the highest strains indicating fluid-like mechanical response. In figure 6.10, we plot the temperature-dependent linear moduli, G'_{l} , defined as the magnitude of G' at very low applied strain amplitudes, and yield stresses, σ_y , for all the suspensions investigated here. We see from figure 6.10(a) that G'_{I} increases with particle stiffness. The yield stresses are calculated from amplitude sweep data following the method proposed by Laurati et al. [39]. The details of the analysis is described in section 2.4.1b(i) of chapter 2 and a representative plot is shown in figure 6.11. From figure 6.10(b), we note that $\sigma_{\rm v}$ values are the lowest for suspensions of soft particles at temperatures near the LCST. Suspensions of soft PNIPAM particles therefore shear melt at smaller stresses and are mechanically very fragile. Interestingly, dense suspensions of PNIPAM particles of intermediate stiffnesses display two-step yielding above the LCST (figure 6.9(f); indicated by vertical dashed lines), resembling the yielding of glasses/gels comprising hard attractive colloidal particles [36]. The first yield point (γ_{y1}) can be attributed to inter-cluster bond breaking of the caged particles constituting the dense suspensions, while the second yield point (γ_{y2}) likely Chapter 6. Role of microgel stiffness in particle self-assembly and suspension rheology across the lower critical solution temperature

arises from the breaking of cages or clusters into smaller fragments [40]. The absence of two-step yielding in suspensions of soft PNIPAM particles above the LCST can be attributed to their relatively lower effective volume fractions. For suspensions of stiffer PNIPAM particles, the highly crowded environment ensures that bond and cage-breaking phenomena coexist simultaneously, resulting in one-step yielding of these suspensions under high strains (figure 6.9(i)). Our strain amplitude sweep data therefore verify our earlier conclusions that suspensions of PNIPAM particles synthesized using higher crosslinker concentrations exhibit characteristics of attractive hard colloidal glasses, while suspensions of soft particles form relatively weaker gels below and above the LCST.

6.3.2c Cryogenic scanning electron microscopy to directly visualize suspension microstructures

One of the key motivations of this study is to probe the mechanical properties of the solid phases of PNIPAM suspensions comprising particles of various stiffnesses over a broad range of temperatures across the LCST. We next attempt to understand our rheology data in terms of the underlying self-assembled colloidal suspension microstructures via direct visualization using a cryogenic scanning electron microscope. In figure 6.12, we show the temperature and stiffness induced morphological changes in dense aqueous suspensions of soft PNIPAM particles ($\alpha = 3.36$; figures 6.12(a-c)), particles with intermediate stiffnesses ($\alpha = 2.00$; figures 6.12(d-f)) and stiff particles $(\alpha = 1.33; \text{ figures } 6.12(\text{g-i})), \text{ prepared at temperatures below LCST } (15^{\circ}\text{C}), \text{ near}$ LCST (33°C) and above LCST (55°C). Additional cryo-SEM micrographs of suspensions of PNIPAM particles of maximum swelling ratios $\alpha = 2.56, 1.51$ and 1.41 are shown in figure 6.13. Dense aqueous suspensions of the relatively softer PNI-PAM particles display three dimensional network structures (figures 6.12(a-f) and 6.13(a-f)). We believe that the networks comprise strands of particles connected to form system-spanning structures displaying gel-like rheology as also reported in earlier studies [39, 41, 42]. We note here that our rheology data (figures 6.8(a-c))



Figure 6.12: Cryo-SEM micrographs of aqueous suspensions of (a-c) soft PNIPAM particles, (d-f) PNIPAM particles of intermediate stiffnesses and (g-i) stiff PNIPAM particles, prepared at temperatures below the LCST, near the LCST and above the LCST respectively, and then frozen to cryogenic temperatures.

and 6.9(a-c)) also indicate gel-like rheology for suspensions of softer particles. In figure 6.8(a), for example, we had observed two characteristic timescales that are presumably set by the motion of single particles on the one hand, and the dynamics of the gel network strands on the other [40].

Inhomogeneous networks are clearly visible in these suspensions at temperatures near and above the LCST (figures 6.12(b-c) and 6.13(b-c)). Above the LCST, the images (figures 6.12(c,f)) reveal the existence of phase separation that is expected to arise due to enhanced hydrophobic interactions between PNIPAM particles. We adopt a protocol used earlier [43] to estimate the average pore areas of the porous microstructures displayed in figures 6.12(a-f) and 6.13(a-f). The presence of vitrified water on the structures can lead to an underestimation of average pore area. How-



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Figure 6.13: Cryo-SEM micrographs of aqueous suspensions of (a-c) soft PNIPAM particles, (d-f) PNIPAM particles of intermediate stiffnesses and (g-i) stiff PNIPAM particles, prepared at temperatures below the LCST, near the LCST and above the LCST respectively, and then frozen to cryogenic temperatures.

ever, since the sublimation time (15 minutes) after cutting the vitrified samples is identical in all the experiments, an equal sublimation-depth is expected for all the samples studied using cryo-SEM. We have estimated the average pore areas only for aqueous PNIPAM suspensions comprising the softer particles where we clearly observe network-like structures (figures 6.12(a-f) and 6.13(a-f)). We see from figure 6.14 that the average pore areas of aqueous PNIPAM suspensions decrease with increase in stiffness of the constituent particles. We note that the larger pore areas for the suspensions constituted by softer particles are indicative of their higher fragilities. As we approach the LCST, the pore areas increase due to the rapid collapse of the PNIPAM particles and reduction in the suspension effective volume fraction. The build-up of interparticle attraction due to enhanced hydrophobic interactions



Figure 6.14: Average pore area vs. temperature T for aqueous suspensions of PNIPAM particles of different maximum swelling ratios α .

above the LCST can explain the decrease in pore sizes at the highest temperatures. For the suspensions constituted by the softest particles, we note that the pore sizes are larger above the LCST than below it. This verifies our rheology observation that the gels formed by these suspensions are comparatively weaker above the LCST. Interestingly, we observe that suspensions of the stiff PNIPAM particles remain in a glassy state at all the temperatures explored here (figures 6.12(g-i) and 6.13(g-i)).

6.4 Conclusions

The present chapter demonstrates that the mechanical properties and self-assembled morphologies of dense PNIPAM suspensions can be tuned by controlling the suspension temperature and particle stiffness. We synthesize PNIPAM particles of different stiffnesses by varying the crosslinker concentration in a free radical precipitation polymerization method. We quantify the stiffnesses of these particles by measuring their maximum swelling ratios. Our dynamic light scattering data reveal that the soft particles, characterized by higher osmotic pressures, deswell more rapidly than stiff particles upon increasing temperature. We perform Fourier transform Chapter 6. Role of microgel stiffness in particle self-assembly and suspension rheology across the lower critical solution temperature

infrared spectroscopy experiments to study the temperature-dependent hydrophobicity of the aqueous PNIPAM suspensions. We observe that the hydrophobicity of PNIPAM particles increase with temperature and decrease with particle stiffness. Interestingly, we observe a non-monotonic increase in the suspension viscoelasticity when temperature is increased across the LCST. We note that suspensions comprising the softest PNIPAM particles exhibit a gel-liquid-gel transition with increase in temperature, with the gel phase above the LCST being significantly weaker than that formed below the LCST. On the other hand, suspensions comprising PNI-PAM microgels with large particle stiffnesses form disordered glassy phases below and above the LCST, while retaining finite though low rigidities at the LCST. An increase in suspension rigidity above the LCST is attributed to a change in interparticle interaction from repulsive to attractive [6] due to enhancement of the hydrophobic nature of the PNIPAM particles with increasing temperature. Cryo-SEM studies to visualize the microscopic suspension structures reveal significant changes in the morphologies of the particle assemblies with a change in suspension temperature and stiffness of the constituent particles. In results that verify our rheology data, we observe that suspensions of soft PNIPAM particles form gel-like networks at temperatures below and above the LCST. Owing to the higher particle hydrophobicities, we even see phase separation at temperatures near and above the LCST. In contrast, suspensions of stiff PNIPAM particles remain in a glassy state at all the experimental temperatures studied here. A glass-liquid-gel transition was reported earlier when temperature of a dense PNIPAM suspension was raised across the LCST [6]. We show here, for the first time to the best of our knowledge, that phase transformations in thermoreversible microgel suspensions depend sensitively on particle stiffness. By tuning just the PNIPAM particle stiffness and suspension temperature, we have successfully achieved a rich variety of suspension phases with

unique properties.

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Since the mechanical properties and microstructures of dense PNIPAM suspensions can be controlled simply by tuning the suspension temperature and stiffnesses of the constituent particles, their aqueous suspensions are potentially good candidates for synthesizing multifunctional materials. The tunability of suspension rheology by controlling particle stiffness and medium temperature can be exploited in designing soft robotic applications, for example, in making microgrippers, or to fold flat gel sheets [44]. Our ability to control the stiffnesses of PNIPAM particles raises the possibility of their use in soft biomimetic machines. The bending or twisting of a flat gel sheet, comprising layers of microgel particle aggregates of different stiffnesses, can, in principle, be achieved by the application of a temperature gradient. PNIPAM microgel suspensions are extremely resilient to tensile and compressive stresses [21] and are also very flexible. Since these materials can be used in various engineering and biomimetic applications, further research on their mechanical properties is of utmost importance.

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Chapter 7

Dichotomous behaviors of stress and dielectric relaxations in dense suspensions of swollen thermoreversible microgel microparticles

7.1 Introduction

Soft materials such as colloidal suspensions, gels, glasses, polymers and biological macromolecules can deform easily under the influence of thermal stresses at room temperature. When subjected to large external shear stresses and strains, they display fascinating flow properties over a hierarchy of spatiotemporal scales [1]. The application of appropriate shear profiles can cause build-up or disruption of fragile suspension structures, in phenomena that are commonly referred to as shear-induced thickening or thinning respectively. It would be of interest to systematically study how a material's microscopic properties dictate its bulk flow behavior. Dielectric spectroscopy, which probes how an externally applied oscillatory electric field interChapter 7. Dichotomous behaviors of stress and dielectric relaxations in dense suspensions of swollen thermoreversible microgel microparticles 173

acts with a material's permanent or field-induced dipoles at different oscillatory frequencies, is a widely used technique to study complex metastable phenomena such as the dynamical slowing down process in glass-forming liquids [2, 3]. The rheodielectric technique, which involves the study of the dielectric response of a material in the presence of shear forces, has been used to directly determine how shearinduced structural changes alter charge distributions and polarization fluctuations in nematic liquid crystals, polymers, electrorheological fluids (ERFs), conducting carbon black suspensions, viscoplastic droplets and elastomers [4–14]. Simultaneous measurements of dielectric and viscoelastic properties can therefore help us to correlate material properties over length and time scales spanning several decades.

In the existing scientific literature, researchers have investigated the temperature dependent phase behavior of aqueous poly(N-isopropylacrylamide) (PNIPAM) suspensions (properties of PNIPAM particles in aqueous suspensions are discussed in details in section 1.6 of chapter 1) using independent rheological and dielectric measurements [15-18]. Romeo *et al.* have reported *via* bulk rheology experiments that PNIPAM particles in dense aqueous suspensions undergo a glass-liquid-gel transition with increase in temperature across the LCST due to changes in the Flory-Huggins parameter [19]. Using UV-visible spectroscopy and thermodynamic perturbation theory, Wu et al. [18] have investigated the temperature dependent phase behavior of aqueous PNIPAM suspensions. While PNIPAM particles were seen to form crystalline structures below the LCST, the suspension liquefied at a temperature near the LCST and phase separated at higher temperatures. Su et al. [20] have systematically studied the dielectric behavior of suspensions of PNIPAM particles of different crosslinker distributions (dense core (DC), loose core (LC) and homogeneously (HOMO) cross-linked particles). While the LCST does not change very much, the dielectric parameters of the aqueous PNIPAM suspensions near the LCST display significant changes with change in the distribution of crosslinkers. Dielectric spectroscopy experiments performed by Young *et al.* [21] have confirmed that dense PNIPAM suspensions exhibit a colloidal crystal to liquid transition upon increasing temperature below the LCST. While most of the previous experimental studies focused exclusively on the rheological or dielectric properties of aqueous PNIPAM suspensions [20–22], rheo-dielectric studies investigating the dielectric response of colloidal microgel suspensions under applied strains have never been reported to the best of our knowledge.

In this chapter, we attempt to bridge this gap by reporting the results of our recent rheo-dielectric experiments, performed to study the dielectric response of PNIPAM colloidal suspensions under large applied deformations for different particle effective volume fractions and suspension temperatures. We synthesize PNIPAM particles using a free radical precipitation polymerization procedure and characterize the thermoresponsive behavior and LCST of these particles in aqueous suspensions using dynamic light scattering (DLS) and differential scanning calorimetry (DSC). In the rheo-dielectric measurements, we apply large amplitude oscillatory strains (LAOS) to the sample while simultaneously measuring their dielectric responses using a precision impedance analyzer. We analyze the real and imaginary parts of the dielectric permittivities of aqueous PNIPAM suspensions of different effective volume fractions, subjected to large applied strain amplitudes, at temperatures below, near and above the LCST over a wide frequency range of the applied electrical voltage. For all the samples investigated in this study, the real parts of the dielectric permittivities display two distinct dielectric relaxation processes in the low and high frequency regimes. We extract the dielectric relaxation strengths and relaxation times at different strain amplitudes by fitting the experimental data to the Cole-Davidson relaxation model [23]. In earlier studies, a low frequency dielectric relaxation process was attributed to segmental motion of the polymers and the motion of counterions along the polymer chain over the entire temperature range [21]. The high frequency dielectric relaxation was understood to originate from counterion fluctuations and interfacial polarization below and above the LCST respectively [21]. Chapter 7. Dichotomous behaviors of stress and dielectric relaxations in dense suspensions of swollen thermoreversible microgel microparticles 175

For densely-packed aqueous PNIPAM suspensions below the LCST, we report that both the real and imaginary contributions of the dielectric permittivities decrease with increase in strain amplitudes. In contrast, the dielectric responses of densely-packed PNIPAM suspensions at temperatures near and above the LCST, and of loosely-packed suspensions at all experimental temperatures, are insensitive to the applied strain. When the applied strain amplitude is increased systematically, we observe significant increases of the dielectric relaxation times of denselypacked suspensions at a temperature below the LCST. This indicates the presence of a counter-intuitive dynamical slowing down process at very short time scales. Interestingly, we also observe a simultaneous speeding up of the stress relaxation process in bulk rheological measurements. Therefore, while our dielectric relaxation data indicates dynamical slowing down at the shortest accessible length scales, our bulk rheological data points to simultaneous shear thinning rheology at macroscopic length scales. We attribute the observed length scale dependent response functions in densely-packed suspensions below the LCST to the shear-induced formation and rupture of clusters of swollen PNIPAM particles. We propose that while the restricted motion of the entangled PNIPAM chains under shear increases the dielectric relaxation time, the shear-induced disruption of the swollen PNIPAM microstructures accelerates the stress relaxation in the bulk. Our study, therefore, provides insights into the dynamics of PNIPAM particles in aqueous suspensions over several decades of length and time scales. Such length scale dependent rheology of sheared densely-packed PNIPAM suspensions can have far-reaching implications in the use of colloidal microgels in electrical energy storage devices such as flow batteries [24] and flow capacitors [25].

7.2 Sample preparation and experimental techniques

Poly(*N*-isopropylacrylamide) (PNIPAM) particles are synthesized using one-pot free radical precipitation polymerization method (discussed in detail in section 2.2.2 of chapter 2). In the synthesis of PNIPAM particles, 7 g of NIPAM, 0.875 g of crosslinker (MBA), 0.03 g of surfactant (SDS) and 0.28 g of initiator (KPS) were used in 500 ml Milli-Q water. After synthesis, the suspensions are purified by 4 successive centrifugation and re-dispersion cycles to remove SDS, the excess monomers, oligomers and other impurities. Centrifugations are performed at speeds of 20,000 RPM for 60 minutes. After centrifugation, the supernatant is removed and the remaining sample is dried by evaporating the water. A fine powder is prepared by grinding the dried particles with a mortar and pestle. Details of preparation of dilute and concentrated samples for dynamic light scattering and rheological measurements are given in chapter 5 and 6. The experimental techniques used in this chapter (DLS, rheology, rheo-dielectric and DSC) are discussed in chapter 2.

7.3 Results and discussion

PNIPAM particles are soft and can deform when packed above the random close packing volume fraction of monodisperse hard spheres. Due to their deformability, the volume fraction ϕ is not the appropriate parameter to quantify the packing of these particles in suspension. Therefore, we use a modified parameter called the effective volume fraction, ϕ_{eff} , as a quantitative measure of the extent of particle packing in suspension. The protocol for computing ϕ_{eff} for suspensions of PNIPAM particles in water is discussed in detail in section 2.4.1a(i) of chapter 2. Figure 7.1 shows the plot of the relative viscosity, η_{rel} vs. the polymer concentration. The data is fitted to the Batchelor's equation [26, 27]. The zero-shear viscosities η_0 of aqueous PNIPAM suspensions were estimated by fitting the η vs. $\dot{\gamma}$ curves to



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Figure 7.1: (a) Relative viscosity $\eta_{rel} vs.$ concentration c of PNIPAM particles in aqueous suspensions. The solid line is a fit to equation 2.14 of chapter 2. The inset shows the plot of the measured suspension viscosities $\eta vs.$ shear rate. The solid lines are fits to the Cross model (equation 2.13 of chapter 2).

equation 2.13 (a representative plot of η versus $\dot{\gamma}$ of PNIPAM suspensions having particle concentrations 1.0, 0.9 and 0.7wt.% is shown in the inset of figure 7.1). The estimated value of polymer concentration inside the particles, c_p , the concentrations and the calculated effective volume fractions of the aqueous PNIPAM suspensions used in this chapter are listed in table 7.1. The lower critical solution temperature (LCST) of the aqueous PNIPAM suspensions was quantified using differential scanning calorimetry (DSC) (Mettler Toledo, DSC 3). The temperature corresponding to the endothermic peak ($\approx 34.3^{\circ}$ C) in figure 2.15 represents the LCST of the PNIPAM particles in their aqueous suspensions. The average sizes and the ther-

$c_p(wt.\%)$	<i>c</i> ((<i>wt</i> .%))	ϕ_{eff}
12.18	23.14	1.9
12.18	19.49	1.6
12.18	15.83	1.3

Table 7.1: Fitted values of the polymer concentration, c_p , inside each particle in the swollen state, PNIPAM particle concentrations, c, that were used, and the effective volume fractions, ϕ_{eff} , of the particles in aqueous suspension.

moreversible swelling-deswelling transition of PNIPAM particles in a dilute aqueous suspension were recorded using dynamic light scattering (DLS) (details of the DLS setup is provided in section 2.3 of chapter 2). We observe that the average hydrodynamic diameter of PNIPAM decreases abruptly when temperature is raised (figure 7.2(a)), thereby signalling a swelling-deswelling transition of the microgel particles. We note that the thermoreversible PNIPAM particles swell maximally below 20°C and collapse fully above 45°C.

We performed dielectric measurements of aqueous PNIPAM suspensions using a precision impedance analyzer (Wayne Kerr Electronics, 6500B series). Figure 7.2(b) displays a schematic diagram of the rheo-dielectric setup. The rheo-dielectric setup has been discussed in details in section 2.5 of chapter 2. Representative plots of the real and imaginary parts of the dielectric permittivity, measured for a PNIPAM suspension of effective volume fraction 1.9 below the LCST under different oscillatory strains, are displayed in figure 7.2(c). In observations that are consistent with previous studies [20, 21], we note that the real part of the dielectric permittivity, ε'_r , exhibits two distinct relaxation processes in the low and high frequency regimes. As discussed earlier in the context of PNIPAM suspensions [21], the relaxation observed at frequencies below approximately 1kHz (the low frequency relaxation) can be attributed to the local segmental motion of the polymer and also to the motion of counterions along the polymer chain over the entire temperature range. Figure 7.3(a) shows a schematic representation of the segmental motion of a PNIPAM chain.



Figure 7.2: (a) DLS measurements of the hydrodynamic diameters of thermoreversible PNIPAM particles during heating and cooling temperature cycles. The different background colors represent the three different regimes showing the distinct temperature dependent responses of the thermoreversible PNIPAM; from left to right: below LCST, near LCST and above LCST, respectively. Dielectric measurements were performed at 20°C, 33°C and 55°C, which are marked with vertical lines. (b) Schematic representation of a rheo-dielectric setup. (c) Dependence of the real part of the relative dielectric permittivity (ε'_r) of an aqueous PNIPAM suspension of volume fraction $\phi_{eff} = 1.9$ on the frequency of the AC electrical voltage for various applied strain amplitudes at 20°C (below the LCST). The solid lines are fits to the real part of equation 7.1. The inset shows the imaginary part of the dielectric permittivity (ε'_r) of an aqueous PNIPAM suspension of volume fraction $\phi_{eff} = 1.9$ for the same applied strain amplitudes at 20°C.



Figure 7.3: Schematic diagram of (a) segmental motion of a PNIPAM chain in an aqueous suspension, represented by a pink arrow, at a temperature below the LCST. (b) Interfacial polarization (at a temperature above the LCST) where the dark blue shell represents the cloud of sulfate ions and the light blue shell represents the cloud of counterions around the collapsed PNIPAM particle.

The relaxation process that we observe at frequencies greater than 1kHz (high frequency dielectric relaxation) in figure 7.2(c) can be attributed to the fluctuations of counterions (due to the motion of Na^+ counterions around the SO_4^- groups dissociated from sodium dodecyl sulphate (SDS) used during PNIPAM synthesis) below the LCST and to interfacial polarization (schematic illustration displayed in figure 7.3(b)) above the LCST [21]. Since PNIPAM particles swell fully by absorbing water at a temperature below the LCST, a clear interface between PNIPAM particles and water does not exist. Therefore, the main contribution to the fast dielectric response below the LCST arises from the electric field-induced displacement and rearrangement of counterions bound to the charged colloidal particles [21]. In contrast, PNIPAM particles collapse and expel most of the absorbed water above the LCST, thereby revealing a clear particle-water interface. Hence, at a temperature above the LCST, interfacial polarization (the separation of counterion charges at the interface) dominates the high frequency relaxation process. The acquired dielectric data has tiny fluctuations presumably arising due to the presence of metallic electrical contacts [7]. In the present work, the raw dielectric permittivity data have been smoothed by averaging over 10 adjacent data points (figure 7.4).

The acquired frequency dependent dielectric permittivity data were fitted to the Cole-Davidson relaxation model by incorporating two relaxation terms that



Figure 7.4: Plots of raw and smoothed data corresponding to the real part of the dielectric permittivity of an aqueous PNIPAM suspension of effective volume fraction ϕ_{eff} = 1.9 at 20°C at an applied strain amplitude of 500%.

correspond to the low and high frequency regimes (the slow and fast relaxation processes respectively), while also accounting for electrode polarization [20, 21]:

$$\epsilon_r^* = \epsilon_h + \frac{\epsilon_l - \epsilon_m}{1 + (j\omega\tau_s)^{\beta_s}} + \frac{\epsilon_m - \epsilon_h}{1 + (j\omega\tau_f)^{\beta_f}} + A\omega^{-m}$$
(7.1)

Here, $\varepsilon_l, \varepsilon_m$ and ε_h are the dielectric permittivities in the low, intermediate and high frequency regimes respectively, τ_s and τ_f are respectively the slow and fast dielectric relaxation times, while β_s and β_f are the corresponding exponents which vary between 0 to 1. It is to be noted that $\Delta \varepsilon_l$ ($=\varepsilon_l - \varepsilon_m$) and $\Delta \varepsilon_h$ ($=\varepsilon_m - \varepsilon_h$) are the dielectric relaxation strengths in the low and high frequency regimes respectively. The term $A\omega^{-m}$, where A and m are adjustable parameters, is introduced to account for electrode polarization (EP) which occurs at lower frequencies due to the accumulation of free charges at the electrode interface. These charged species presumably originate from the electrolyte (potassium persulfate KPS) that we employed as a reaction initiator during the synthesis process.

Figure 7.5 shows three-dimensional representations of the real and imaginary parts of the dielectric permittivities of aqueous poly(N-isopropylacrylamide) (PNIPAM)



Figure 7.5: Three dimensional representations at 20°C (below the LCST) of the (a) real (ε_r') and (b) imaginary (ε_r'') parts of the relative dielectric permittivities of aqueous PNIPAM suspensions of effective volume fraction $\phi_{eff} = 1.9$, (c) ε_r' and (d) ε_r'' for effective volume fraction $\phi_{eff} = 1.6$, and (e) ε_r' and (f) ε_r'' for effective volume fraction $\phi_{eff} = 1.3$, over a range of AC electrical voltage frequencies and applied oscillatory strains. The color bars represent the values of ε_r' and ε_r'' with their magnitudes increasing from bottom to top.



Figure 7.6: Storage moduli (G') of aqueous suspensions of PNIPAM particles of different effective particle volume fractions at temperatures (a) 20°C, (b) 33°C and (c) 55°C as a function of applied oscillatory strains. The frequency of oscillation is kept constant at 10rad/sec.

suspensions at 20° C (below the LCST) vs. frequency of the applied alternating electrical voltage and the applied strain amplitude. At very low strains and at a temperature below the LCST, the elasticities of PNIPAM suspensions of the higher effective volume fractions ($\phi_{eff} = 1.9$ and 1.6) are comparable to each other, but are very different from the sample of the lowest effective volume fraction (ϕ_{eff} = 1.3) used here (figures 7.6). We designate the samples of $\phi_{eff} = 1.9$ and 1.6 as densely-packed suspensions and the one of $\phi_{eff} = 1.3$ as a loosely-packed suspension. Figures 7.7 and 7.8 respectively show three-dimensional representations of the dielectric permittivities as functions of strain amplitudes and AC electrical voltage frequencies for the densely-packed and loosely-packed aqueous PNIPAM suspensions at temperatures 33° C (near the LCST) and 55° C (above the LCST). From figures 7.5(a-d), we note that both real and imaginary dielectric permittivities decrease with increasing applied strain amplitudes for the densely-packed PNIPAM suspensions ($\phi_{eff} = 1.9$ and 1.6) below the LCST. The observed decreases in ε_r' and ε_r'' due to an increase in applied strains can be attributed to enhanced structural deformations of the swollen PNIPAM particles in aqueous suspensions at high effective volume fractions. The color bars in figures 7.5, 7.7 and 7.8 represent the values of $\varepsilon_{r}^{'}$ and $\varepsilon_{r}^{''}$ with their magnitudes increasing from bottom to top. We observe that for the loosely-packed PNIPAM suspension, the dielectric permittivities are insensitive to the applied strain amplitude at all temperatures (figures (e-f) of 7.5, 7.7



Figure 7.7: Three dimensional representations at 33°C (near the LCST) of the (a) real (ε'_r) and (b) imaginary (ε''_r) parts of the relative dielectric permittivities of aqueous PNIPAM suspensions of effective volume fraction $\phi_{eff} = 1.9$, (c) ε'_r and (d) ε''_r for effective volume fraction $\phi_{eff} = 1.6$, and (e) ε'_r and (f) ε''_r for effective volume fraction $\phi_{eff} = 1.3$, over a range of AC electrical voltage frequencies and applied oscillatory strains. The color bars represent the values of ε'_r and ε''_r with their magnitudes increasing from bottom to top.



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Figure 7.8: Three dimensional representations at 55°C (above the LCST) of the (a) real (ε'_r) and (b) imaginary (ε''_r) parts of the relative dielectric permittivities of aqueous PNIPAM suspensions of effective volume fraction $\phi_{eff} = 1.9$, (c) ε'_r and (d) ε''_r for effective volume fraction $\phi_{eff} = 1.6$, and (e) ε'_r and (f) ε''_r for effective volume fraction $\phi_{eff} = 1.3$, over a range of AC electrical voltage frequencies and applied oscillatory strains. The color bars represent the values of ε'_r and ε''_r with their magnitudes increasing from bottom to top.



Figure 7.9: AC electrical voltage frequency dependence of the real parts of the relative dielectric permittivities (ε'_r) for aqueous PNIPAM suspensions of effective volume fractions $\phi_{eff} = 1.9$ at temperatures (a) 20°C, (b) 33°C, (e) 55°C, for effective volume fraction $\phi_{eff} = 1.6$ at temperatures (d) 20°C, (e) 33°C, (f) 55°C and and for effective volume fraction $\phi_{eff} = 1.3$ at temperatures (g) 20°C, (h) 33°C, and (i) 55°C. The solid lines are the fits to the real part of equation 7.1.

and 7.8). For the densely-packed PNIPAM suspensions, in contrast, the real and imaginary permittivities are independent of the applied shear only at temperatures near and above the LCST (figures (a-d) of 7.7 and 7.8). For significant modifications in the dielectric properties of homogeneous polymeric systems, the applied deformation must be greater than the equilibrium molecular motion (shear rate > relaxation time⁻¹) [5, 7]. Small deformations can affect the dielectric properties of glassy systems due to the presence of dynamically heterogeneous structures [5, 7]. Our results indicate that densely-packed PNIPAM suspensions at a temperature below the LCST are possibly in a disordered and metastable (glassy) state consti-

	1				1							
		$20^{\circ}C$				33°C				55°C		
$\gamma(\%)$	A	Aerror	т	m _{error}	A	Aerror	т	m _{error}	A	Aerror	т	m _{error}
0	3.9×10^{7}	7.1×10^{6}	0.51	0.05	3.9×10^{7}	4.5×10^{6}	0.48	0.032	5.7×10^{7}	3.0×10^{6}	0.46	0.01
10	3.7×10^{7}	7.0×10^{6}	0.51	0.05	3.9×10^{7}	4.6×10^{6}	0.47	0.03	6.1×10^{7}	3.0×10^{6}	0.47	0.01
50	3.6×10^{7}	9.8×10^{6}	0.52	0.07	3.9×10^{7}	4.4×10^{6}	0.47	0.03	6.6×10^{7}	3.7×10^{6}	0.48	0.01
100	3.4×10^{7}	9.2×10^{6}	0.52	0.07	3.3×10^{7}	5.2×10^{6}	0.44	0.04	5.7×10^{7}	4.2×10^{6}	0.44	0.02
500	2.5×10^{7}	4.1×10^{6}	0.59	0.04	3.2×10^{7}	4.9×10^{6}	0.44	0.04	5.8×10^{7}	4.0×10^{6}	0.99	0.07
1000	1.6×10^{7}	6.3×10^{6}	0.71	0.09	3.0×10^{7}	6.7×10^{6}	0.46	0.05	6.0×10^{7}	4.9×10^{6}	0.47	0.09
1200	1.3×10^{7}	4.5×10^{6}	0.73	0.08	3.2×10^{7}	3.7×10^{6}	0.43	0.03	8.5×10^{7}	9.1×10^{6}	0.55	0.02
1500	2.6×10^{7}	2.0×10^{6}	1.06	0.17	3.1×10^{7}	2.1×10^{6}	0.42	0.01	7.2×10^{7}	5.8×10^{6}	0.47	0.02
2000	9.4×10^{7}	6.1×10^{6}	0.86	0.19	3.6×10^{7}	5.9×10^{6}	0.46	0.04	7.5×10^{7}	8.5×10^{6}	0.52	0.02

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Table 7.2: Values of parameters A and m at different temperatures explored in this study, extracted by fitting the ε'_r data of aqueous PNIPAM suspensions having effective volume fraction $\phi_{eff} = 1.9$ to equation 7.1.

tuted by PNIPAM particle assemblies. For the loosely-packed aqueous PNIPAM suspension at all temperatures and the densely-packed suspensions at temperatures near or above the LCST, the observed insensitivity of the dielectric responses to applied deformations presumably arises because of an absence of self-assembled particle aggregates. Smaller particle assemblies have much higher relaxation rates and therefore require much larger shears to induce appreciable changes in the dielectric properties, hence the observed insensitivity of the measured dielectric responses to applied shears in the last scenario.

The real parts of the dielectric permittivities of aqueous PNIPAM suspensions show two distinct dielectric relaxation processes in the low and high frequency regimes, as can be clearly seen in (a), (c) and (e) of figure 7.5, 7.7 and 7.8. We compute the relaxation times and dielectric strengths (determined by the number density of molecules, magnitudes of the dipole moments and orientation fluctuations of the dipoles [4, 5]) of all the PNIPAM suspensions prepared at temperatures below, near or above the LCST, by fitting the acquired ε'_r data to the real part of equation 7.1 (fitted data are shown in figure 7.9). The dielectric strengths and relaxation times provide important information about the orientation and dynamics

		20°C				33°C				55°C		
$\gamma(\%)$	A	Aerror	т	m _{error}	Α	Aerror	т	m _{error}	Α	Aerror	т	m _{error}
0	3.1×10^{7}	3.2×10^{6}	0.50	0.02	3.6×10^{7}	1.9×10^{6}	0.48	0.01	4.1×10^{7}	2.3×10^{6}	0.44	0.01
10	3.6×10^{7}	3.3×10^{6}	0.54	0.02	3.6×10^{7}	2.0×10^{6}	0.48	0.01	4.1×10^{7}	2.3×10^{6}	0.45	0.01
50	3.0×10^{7}	4.0×10^{6}	0.50	0.03	3.5×10^{7}	2.0×10^{6}	0.48	0.01	3.8×10^{7}	3.2×10^{6}	0.43	0.02
100	2.9×10^{7}	3.1×10^{6}	0.50	0.02	3.5×10^{7}	2.2×10^{6}	0.48	0.01	3.9×10^{7}	2.3×10^{6}	0.43	0.01
500	2.3×10^{7}	6.2×10^{6}	0.53	0.07	3.4×10^{7}	2.3×10^{6}	0.47	0.01	2.7×10^{7}	1.0×10^{6}	0.38	0.01
1000	1.6×10^{7}	7.3×10^{6}	0.69	0.14	3.4×10^{7}	1.9×10^{6}	0.46	0.01	3.38×10^{7}	1.9×10^{6}	0.41	0.01
1200	1.3×10^{7}	8.5×10^{6}	0.78	0.16	3.4×10^{7}	4.1×10^{6}	0.47	0.03	3.2×10^{7}	2.6×10^{6}	0.40	0.02
1500	2.0×10^{6}	7.5×10^{5}	0.55	0.09	2.7×10^{7}	3.5×10^{6}	0.42	0.03	3.7×10^{7}	4.0×10^{6}	0.45	0.03
2000	1.1×10^{7}	5.3×10^{6}	0.9	0.03	2.75×10^{7}	1.8×10^{6}	0.43	0.02	4.2×10^{7}	4.3×10^{6}	0.48	0.02

Table 7.3: Values of parameters A and m at different temperatures explored in this study, extracted by fitting the ε'_r data of aqueous PNIPAM suspensions having effective volume fraction $\phi_{eff} = 1.6$ to equation 7.1.

					1							
		$20^{\circ}\mathrm{C}$				33°C				$55^{\circ}C$		
$\gamma(\%)$	A	A_{error}	т	m _{error}	A	A _{error}	т	m _{error}	Α	A _{error}	т	m _{error}
0	3.6×10^{7}	3.6×10^{6}	0.54	0.02	3.8×10^{7}	2.1×10^{6}	0.51	0.01	4.5×10^{7}	1.2×10^{6}	0.49	0.01
10	3.6×10^{7}	3.8×10^{6}	0.54	0.03	5.2×10^{7}	3.6×10^{6}	0.6	0.02	4.1×10^{7}	1.3×10^{6}	0.47	0.01
50	3.5×10^{7}	4.4×10^{6}	0.54	0.03	4.1×10^{7}	3.2×10^{6}	0.52	0.02	4.1×10^{7}	2.2×10^{6}	0.47	0.02
100	3.5×10^{7}	3.3×10^{6}	0.54	0.03	3.2×10^{7}	2.1×10^{6}	0.49	0.01	4.0×10^{7}	1.2×10^{6}	0.47	0.01
500	3.0×10^{7}	3.9×10^{6}	0.52	0.03	2.7×10^{7}	3.2×10^{6}	0.48	0.03	2.9×10^{7}	1.7×10^{6}	0.43	0.01
1000	3.6×10^{7}	3.1×10^{6}	0.56	0.02	3.0×10^{7}	1.8×10^{6}	0.46	0.01	3.0×10^{7}	1.7×10^{6}	0.41	0.01
1200	2.8×10^{7}	3.6×10^{6}	0.53	0.03	2.7×10^{7}	1.7×10^{6}	0.45	0.02	3.1×10^{7}	4.6×10^{6}	0.46	0.04
1500	2.9×10^{7}	5.5×10^{6}	0.52	0.05	2.5×10^{7}	3.4×10^{6}	0.46	0.04	4.6×10^{7}	6.0×10^{6}	0.53	0.03
2000	2.7×10^{7}	2.8×10^{6}	0.51	0.02	3.8×10^{7}	2.7×10^{6}	0.52	0.02	3.4×10^{7}	3.5×10^{6}	0.47	0.02

Table 7.4: Values of parameters A and m at different temperatures explored in this study, extracted by fitting the ε'_r data of aqueous PNIPAM suspensions having effective volume fraction $\phi_{eff} = 1.3$ to equation 7.1.



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Figure 7.10: (a) Low frequency $(\Delta \varepsilon_l)$ and (b) high frequency $(\Delta \varepsilon_h)$ dielectric relaxation strengths and (c) slow (τ_s) and (d) fast (τ_f) relaxation times as functions of applied oscillatory strain amplitudes for aqueous suspensions of PNIPAM of volume fraction ϕ_{eff} = 1.9 at temperatures below, near and above the LCST. These values are obtained by fitting the data in figures 7.5(a), 7.7(a) and 7.8(a) to the real part of equation 7.1.

of the PNIPAM particles under shear flow. It has been reported that the alignment of dipoles parallel and perpendicular to the electric field respectively increase and decrease the measured dielectric strengths [4]. The values of the fitted parameters in the electrode polarization term (A and m) of equation 7.1, which originates from the mobility of the free ions and contributes to the low frequency dielectric permittivities, are listed in tables 7.2-7.4. In figures 7.10(a-b) and 7.11(a-b), we show the low- and high frequency dielectric relaxation strengths ($\Delta \varepsilon_l$ and $\Delta \varepsilon_h$ respectively) of densely-packed PNIPAM suspensions ($\phi_{eff} = 1.9$ in figures 7.10(a-b) and ϕ_{eff} = 1.6 in figures 7.11(a-b)) at all the experimental temperatures. Figures 7.12(ab) display the values of $\Delta \varepsilon_l$ and $\Delta \varepsilon_h$ when oscillatory strains were applied to the



Figure 7.11: (a) Low frequency $(\Delta \varepsilon_l)$ and (b) high frequency $(\Delta \varepsilon_h)$ dielectric relaxation strengths and (c) slow (τ_s) and (d) fast (τ_f) relaxation times as functions of applied oscillatory strain amplitudes for aqueous suspensions of PNIPAM of volume fraction ϕ_{eff} = 1.6 at temperatures below, near and above the LCST. These values are obtained by fitting the data in figures 7.5(c), 7.7(c) and 7.8(c) to the real part of equation 7.1.

loosely-packed PNIPAM suspension ($\phi_{eff} = 1.3$) at the same temperatures. For all the PNIPAM suspensions, $\Delta \varepsilon_l$, which is understood to originate from the segmental motion of PNIPAM chains over the entire temperature range as reported in an earlier work [21], shows an enhancement with increasing suspension temperatures. This can be attributed to the increase in polymer density inside the PNIPAM particles due to particle shrinkage/ collapse above the LCST. Interestingly, we note that both $\Delta \varepsilon_l$ and $\Delta \varepsilon_h$ decrease strongly with increase in applied strain amplitudes for densely-packed PNIPAM suspensions at a temperature below the LCST. It has been proposed that the application of shear strain disrupts the structured polymer particles [4] that are present in densely-packed (jammed) suspensions and randomizes the directions of the dipoles. Strong shears are expected to result in the alignment



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Figure 7.12: (a) Low frequency $(\Delta \varepsilon_l)$ and (b) high frequency $(\Delta \varepsilon_h)$ dielectric relaxation strengths and (c) slow (τ_s) and (d) fast (τ_f) relaxation times as functions of applied oscillatory strain amplitudes for aqueous suspensions of PNIPAM of volume fraction ϕ_{eff} = 1.3 at temperatures below, near and above the LCST. These values are obtained by fitting the data in figure 7.5(e), 7.7(e) and 7.8(e) to the real part of equation 7.1.

of dipoles parallel to the flow direction. In our experimental geometry, the flow direction is perpendicular to the electric field. The application of appropriately high shears orients the dipoles along the flow direction and results in the observed decrease in net polarization and dielectric strengths. In contrast, no significant strain-induced changes in $\Delta \varepsilon_l$ and $\Delta \varepsilon_h$ are observed for loosely-packed PNIPAM suspension at all experimental temperatures and for densely-packed PNIPAM suspensions at temperatures near and above the LCST. The strain insensitivity of the dielectric strengths under these conditions arises as the PNIPAM particles do not self-assemble to form strong structures due to low effective volume fractions. We therefore conclude that the packing densities and temperature dependent morphological changes of PNIPAM particles effectively control the dielectric properties and shear responses of their aqueous suspensions.

Apart from the dielectric strength, the other parameters that we study to quantify the responses of the charged species are the fast and slow relaxation times [20, 21], extracted by fitting the observed two-step decay of the real part of the dielectric permittivities to the real part of equation 7.1. Figures 7.10(c-d) and 7.11(c-d) display the slow (τ_s) and fast (τ_f) relaxation times of densely-packed aqueous PNIPAM suspensions at $\phi_{eff} = 1.9$ and 1.6 respectively as a function of strain amplitudes at all the temperatures explored in this study. Figures 7.12(c-d) represent the slow and fast relaxation times as a function of strain amplitude for the loosely-packed PNIPAM suspension (i.e. $\phi_{eff} = 1.3$) at the same temperatures. We see that both τ_s and τ_f decrease with increase in suspension temperature for all the samples at a fixed effective volume fraction. We attribute the observed decrease in time scales with increasing temperatures to the reduction in effective volume fractions and the consequent enhancement of mobilities of the collapsed PNIPAM particles [28]. Interestingly, we see from figures 7.10(c-d) and figures 7.11(c-d) that τ_s and τ_f increase monotonically with increasing strain amplitudes for the densely-packed PNIPAM suspensions at a temperature below the LCST, thereby demonstrating a slowdown of the polarization fluctuation dynamics with increasing strain amplitude. However, the dielectric relaxation time scales of these samples are insensitive to the applied shear at temperatures near and above the LCST where the particles have already collapsed due to expulsion of water. Furthermore, we note that τ_s and τ_f are relatively unaffected by the applied strain amplitudes at all temperatures when PNIPAM particles are loosely-packed in aqueous suspension (figures 7.12(c-The time scales extracted from our rheo-dielectric measurements therefore d)). reveal the distinct dynamical properties of PNIPAM particles in aqueous suspensions at different temperatures and under different externally imposed mechanical stresses.

Moreover, from figures 7.5, 7.7 and 7.8, we observe that the imaginary contributions to the dielectric permittivities show a single loss peak. Figures 7.13(a-c)



Figure 7.13: Relaxation times, τ , estimated from the dielectric loss spectrum for aqueous PNIPAM suspensions of effective volume fractions $\phi_{eff} = (a) 1.9$, (b) 1.6 and (c) 1.3 at temperatures below, near and above the LCST.

show the relaxation times estimated from the peak frequency values of the dielectric losses ($\tau = 1/2\pi f_{peak}$), where f_{peak} is the frequency at which the dielectric loss peak is noted. We see that the relaxation times τ are of the order of the fast relaxation time scales estimated from fits of the real part of the dielectric permittivities to the Cole-Davidson relaxation model (figures 7.10(d) and 7.11(d)). We therefore conclude that the dominant relaxation mechanism responsible for the observed dielectric loss below the LCST originates from counterion polarization. In contrast, at temperatures above the LCST, the dielectric loss can be attributed to interfacial polarization generated by the free charged species present in the suspension and the dynamics of counterions around the particles. In results that are consistent with data displayed in figure 7.10(d) and 7.11(d), we note from figures 7.13(a-b) that the dielectric relaxation times, τ , of densely-packed PNIPAM suspensions (ϕ_{eff} = 1.9 and 1.6) increase with increase in applied strain amplitudes at a temperature below the LCST. However, the relaxation rates are independent of temperature for densely-packed PNIPAM suspensions at temperatures near and above the LCST and for the loosely-packed suspension ($\phi_{eff} = 1.3$) at all temperatures.

To complement our rheo-dielectric study that uncovers counter-intuitive polarization fluctuation dynamics upon applying oscillatory shear deformations, we next study the influence of applied large amplitude oscillatory strains on the bulk mechanical moduli of PNIPAM suspensions by performing independent stress relaxation



Figure 7.14: Oscillatory shear stress response *vs.* time for PNIPAM suspensions of effective volume fractions $\phi_{eff} = 1.9$ at temperatures (a) below LCST (b) near LCST (c) above LCST, $\phi_{eff} = 1.6$ at (d) below LCST (e) near LCST (f) above LCST and $\phi_{eff} = 1.3$ at (g) below LCST (h) near LCST (i) above LCST for different applied oscillatory strains γ .

experiments. In these measurements, the range of the large amplitude oscillatory strains is comparable to that applied in our rheo-dielectric experiments. Our experimental design therefore allows us to study the responses of PNIPAM suspensions over a length scale range varying over several (7-8) orders of magnitude. Stress relaxation decays, exhibited by densely-packed (i.e. $\phi_{eff} = 1.9$ and 1.6) and looselypacked (i.e. $\phi_{eff} = 1.3$) aqueous PNIPAM suspensions at temperatures below, near and above the LCST, upon the application of oscillatory strains of pre-determined amplitudes, are shown in figures 7.14(a,d,g), 7.14(b,e,h), and 7.14(c,f,i), respec-



Figure 7.15: Stress relaxation times, τ_1 , of densely-packed aqueous suspensions of PNI-PAM particles at temperatures 20°C and 55°C as a function of applied oscillatory strain amplitude.

tively. For the densely-packed PNIPAM suspensions at/near the LCST, power-law stress relaxations are observed (figures 7.14(b,e)). For the loosely-packed suspension under the same condition, the stress decay flattens out very rapidly (figure 7.14(h)). Interestingly, the two-step stress relaxation processes observed for the densely-packed PNIPAM suspensions (figures 7.14(a,d) and 7.14(c,f)) below and above the LCST are reminiscent of the relaxation of glassy materials or entangled polymeric melts [29, 30]. Given the extremely rapid decay of the short-time stress relaxation, we could not acquire adequate reliable data to model the fast stress relaxation process satisfactorily. We therefore focus only on the slow bulk stress relaxation data which is well described by the Kohlrausch–Williams–Watts (KWW) model [31]. The KWW model represents the time dependent stress relaxation of the slower mode in glassy materials as a stretched exponential function:

Y (%)



Figure 7.16: A schematic illustration of a densely-packed PNIPAM suspension under an applied strain. The green arrow at the top and the red arrow on the left represent, respectively, the increase in applied strain amplitude and the direction of the electric field.

$$\sigma(\tau) = Aexp[-(\tau/\tau_1)^{\beta}]$$
(7.2)

where, $\sigma(\tau)$, A, τ_1 and β are the time dependent shear stress, intercept of the slow relaxation decay, time scale corresponding to the slow mode of the stress relaxation process and stretching exponent ($0 < \beta < 1$) respectively. We note that the stress relaxation times for densely-packed PNIPAM suspensions, which are obtained by fitting the data plotted in figures 7.14(a,d) to equation 7.2, decrease with applied shear strain amplitude below the LCST (figure 7.15), thereby revealing the presence of bulk shear thinning behavior at low temperatures. Interestingly, therefore, while the polarization fluctuation in a suspension of densely-packed PNIPAM particles slows down with an increase in the applied strain below the LCST, the bulk stress relaxation speeds up simultaneously.

The observed dichotomous dynamics at macroscopic and nanometer length scales can be understood by considering the shear-induced formation and rupture of fragile PNIPAM particle clusters in densely-packed suspensions. It has been reported in Chapter 7. Dichotomous behaviors of stress and dielectric relaxations in dense suspensions of swollen thermoreversible microgel microparticles 197

earlier work that PNIPAM particles in dense aqueous suspensions phase separate by forming clusters under shear flow [28, 32]. We attribute the slowing down of the slow and fast dielectric relaxation processes to the formation of such microscopic PNIPAM particle clusters. This is illustrated in figure 7.16 which schematically represents polarization fluctuations in the sample (left-panel) and breakup of PNIPAM clusters (right-panel) due to stresses imposed by electric fields and shear strains respectively. Badiger et al. [28] have observed stress overshoots in aqueous suspensions of PNIPAM particles undergoing shear flow due to the presence of entangled PNI-PAM polymers. Such shear-induced entanglements of PNIPAM chains in denselypacked suspensions below the LCST are expected to restrict the segmental motion of PNIPAM chains, resulting in the observed increase of the slow dielectric relaxation times. Furthermore, counterion separation is enhanced due to the fragmentation of particle clusters undergoing shear deformation (figure 7.16, right-hand panel). This enhances the particle dipole moments and causes the dielectric fast relaxation processes to slow down. The simultaneous decrease in the dielectric strengths with increasing shears arises from the randomization of the dipoles and the distortions and breakups of PNIPAM clusters by the applied shear. Furthermore, the decrease in the bulk viscosity of PNIPAM suspensions due to shear induced breakdown of the fragile clusters results in accelerated particle dynamics and shear thinning at macroscopic length scales.

7.4 Conclusions

The bulk mechanical response and the polarization fluctuations of sheared complex fluids have independently been studied in the literature using rheometry and dielectric spectroscopy [15–22]. However, to the best of our knowledge, systematic rheo-dielectric experiments have never been performed to study the dynamics of dense colloidal suspensions over spatiotemporal scales spanning several decades. Our work attempts to bridge this gap by simultaneously studying the dielectric and stress relaxation behaviors of aqueous suspensions of colloidal microgel poly(Nisopropylacrylamide) (PNIPAM) particles under large applied oscillatory shear strains. We observe two distinct dielectric relaxation processes in the low and high frequency regimes. The low frequency relaxation process is understood to originate from the segmental motion of the polymer and the motion of counterions along the polymers chains [21] over the entire temperature range. On the other hand, the high frequency relaxation is believed to arise from counterion fluctuations at a temperature below the LCST and from interfacial polarization above the LCST. We propose that the observed decrease of the dielectric relaxation strengths in densely-packed PNIPAM suspensions upon the application of oscillatory shear strains at a temperature below the LCST is due to the distortion of dynamically heterogeneous suspension structures and randomization in the orientations of the constituent dipoles. Notably, the dielectric responses of loosely-packed PNIPAM suspensions at all temperatures and densely-packed PNIPAM suspensions at temperatures near and above the LCST are insensitive to the applied deformations. The most significant finding of this study is that while the polarization fluctuations of densely-packed PNIPAM suspensions slow down with increase in applied oscillatory strain amplitudes at a temperature below the LCST, the bulk stress relaxation dynamics speed up under identical conditions. Earlier studies such as those by Su *et al.* [20] and Yang *et* al. [21] reported the dielectric behavior of relatively dilute aqueous PNIPAM suspensions (0.005 wt.% and 5.6 wt.% respectively). The dielectric strengths and time scales reported in the present study are therefore much higher than for the relaxation dynamics reported earlier [20, 21]. The dense PNIPAM suspensions in our experiments are characterized by a significantly enhanced number of dipoles that restrict the segmental motion of PNIPAM chains, resulting in the novel dynamics reported in our study.

Although the rheo-dielectric technique has been extensively used in the literature to study the dynamics of diverse soft materials such as liquid crystals, polymers, visChapter 7. Dichotomous behaviors of stress and dielectric relaxations in dense suspensions of swollen thermoreversible microgel microparticles 199

coplastic droplets and elastomers [2–8, 13, 14], it has never been used to investigate dense colloidal microgel systems such as PNIPAM suspensions. The present study uncovers the dynamics of a colloidal microgel suspensions over length and time scales spanning 7-8 decades using a single technique. Besides revealing rich dynamical behavior of dense suspensions of PNIPAM microgels at different length scales, we have shown that the self-assembly and dynamical properties of their dense suspensions can be fine-tuned by controlling temperature and the applied strain deformation. These microgels are therefore attractive candidates for engineering energy storage devices, such as stretchable and soft batteries, flow batteries [24] and flow capacitors [25]. We strongly believe that the present study can serve as a starting point for further research into the rheo-dielectric properties of dense colloidal (soft glassy) suspensions.

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Chapter 8

Rheological study of aqueous suspensions of thermoresponsive core-shell particles

8.1 Introduction

The properties of smart or responsive materials can be modified by external stimuli such as pH, stresses and temperature in a controlled and reversible manner. Colloidal microgel particles (microgels) based smart materials have been intensively studied in the literature due to their potential applications as photonic materials, intelligent substrates, in biotechnological applications and drug delivery, etc [1–3]. In addition to their wide applicability, such materials can also be used as models to study complex phenomena, such as the glass transition in colloids [4, 5]. The most extensively studied thermoresponsive microgels is poly(*N*-isopropylacrylamide) (PNI-PAM), which shows a lower critical solution temperature (LCST) at $\approx 34^{\circ}$ C [6, 7]. The thermoresponsive, rheological and phase behavior of PNIPAM particles in dense aqueous suspensions are discussed in detail in chapters 1, 5, 6 and 7. Several articles have reviewed microgel properties and applications during the past decade [8–11]. Thermoresponsive core-shell particles with shells having lower LCST than the cores, first reported by Zeiser *et al.* [12], exhibit qualitatively different swelling behavior, including linear swelling over a broad range of temperatures. Coreshell particles reported by Zeiser *et al.* [12] constitute shell made of poly(*N*-n-propylacrylamide) (PNNPAM) with LCST of $\approx 21^{\circ}$ C and core made of poly(n-iso-propylmethacrylamide) (PNIPMAM) polymers with LCST $\approx 44^{\circ}$ C. The combination of different monomers forming the particle's core and shell provides a large LCST gap of 23°C between the core and shell. Due to such a large LCST gap, these particles exhibit linear swelling behavior between temperatures 25°C and 41°C [12, 13]. Lars *et al.* [14] have studied the swelling behavior of these thermore-sponsive core-shell particles using FTIR spectroscopy. They have observed that the internal structures of these particles are governed by a copolymer-like interaction of core and shell polymers.

Using small-angle neutron scattering, Cors *et al.* [15] have studied the structure of PNIPMAM-core and PNNPAM-shell microgels in aqueous suspensions. They have reported that the internal structures of core and shell are heterogeneous and strongly interpenetrated, which allows linear swelling behavior of these microgel particles. While linear swelling and structural properties of these core-shell particles in dilute aqueous suspensions have been investigated using different experimental techniques, the bulk rheological properties of dense suspensions of these particles have not been studied in the literature to the best of our knowledge.

In this chapter, we study the linear and non-linear rheological behavior of dense aqueous suspensions of thermoresponsive core-shell (PNIPMAM-core (LCST = 44° C) and PNNPAM-shell (LCST = 21° C)) particles. We synthesize core-shell particles using a two-step free radical precipitation polymerization method by following the protocols reported earlier [12]. We use nuclear magnetic resonance (NMR) spectroscopy to confirm the presence of the amide group in the shell monomer (NNPAM). After the synthesis, core-shell particles are visualized by scanning electron microscopy (SEM). The thermoresponsive behavior of these particles in aqueous suspensions is investigated by estimating their hydrodynamic diameter as a function of temperature using dynamic light scattering (DLS). The mechanical properties of dense suspensions of these particles are studied in oscillatory rheology experiments. Finally, non-linear rheological properties of core-shell particles in dense aqueous suspensions are studied by analyzing Lissajous curves.

8.2 Sample preparation and experiment techniques

N-n-propylacrylamide (NNPAM) monomer (shell monomer, $LCST = 21^{\circ}C$) is synthesized using Schotten-Baumann reaction, which is used to synthesize amides from amines and acid chloride, as described elsewhere [16]. Figure 8.1 shows 1H NMR spectroscopy data of the NNPAM monomer. The peak shown by the arrow in figure 8.1 confirms the presence of the amide (NH) group in the NNPAM monomer. Thermoresponsive core-shell particles with a shell consisting of poly(N-npropylacrylamide) (PNNPAM) and a core made of poly(n-iso-propylmethacrylamide) (PNIPMAM) polymers are synthesized using two-step free radical precipitation polymerization method. The synthesis procedure of the shell monomer and coreshell particles is discussed in detail in section 2.2.3 of chapter 2. In the synthesis of core particles, 4.16 g of NIPMAM, 0.504 g of crosslinker (MBA), 0.128 g of surfactant (SDS) and 0.248 g of initiator (APS) were used in 400 mL Milli-Q water. On the other hand, 0.6 g of core particles (PNIPMAM), 2.08 mL of NNPAM, 0.048 g of MBA, 0.128 g of SDS and 0.248 g of initiator (APS) were used to synthesize coreshell particles in 200 mL Milli-Q water. Aqueous suspensions of core-shell particles were prepared by adding a powder of these particles in Milli-Q water. The experimental techniques used in this chapter (DLS, SEM and rheology) are described in chapter 2.





Figure 8.1: 1H NMR spectroscopy data of N-n-propylacrylamide (NNPAM) monomer. The purple arrow indicates the peak corresponding to the amide (NH) group present in the monomer.

8.3 Results and discussions

Figure 8.2(a) shows the SEM image of thermoresponsive core-shell particles in dry form. The core-shell structure of the particles can be seen in figure 8.2(a). We measured the average hydrodynamic diameter of these particles using dynamic light scattering (DLS) within a temperature range between 8°C and 60°C. Figure 8.2(b) represents the hydrodynamic diameters of thermoresponsive core-shell particles as a function of temperature. We observed that core-shell particles swell maximally below $\approx 20^{\circ}$ C (below the LCST of shell particles) and shrink fully above $\approx 44^{\circ}$ C (above the LCST of core particles). As reported earlier [12], we also observed a linear decrease in the diameter of these particles while increasing temperature in



Figure 8.2: (a) Scanning electron micrograph of core-shell particles in the dry state. (b) Average hydrodynamic diameter $\langle d_h \rangle$ as a function of temperature *T* of core-shell particles in dilute suspensions measured using DLS.

the range between $\approx 25^{\circ}$ C and $\approx 40^{\circ}$ C (shown by vertical blue lines in figure 8.2(b)). The size of these particles decreases with increase in temperature as we approach the LCST of the shell particles (21°C) up to 25°C. This is because of increase in hydrophobicity of thermoresponsive shell particles at temperature above the LCST (21°C). At temperature 25°C, shell particles collapse and touches the core particles. Between temperatures 25°C and 40°C, shell particles compress the core, which results in the observed linear change in the size of core-shell particles. At temperatures above 40°C which, is near the LCST of core particles, we note a small decrease in the size of core-shell particles. This is because, at these temperatures, the core particles are already compressed by the shells.

As discussed in earlier chapters (5, 6, 7), thermoresponsive microgels are soft and deformable, and volume fraction ϕ can not be used to quantify their packing in dense aqueous suspensions. Therefore, we use a modified parameter called effective volume fraction ϕ_{eff} . Figure 8.3 shows the plot of relative viscosity as a function of particle concentration. The protocol of estimating the effective volume fraction of soft deformable particles using figure 8.3 is described in section 2.4.1a(i) of chapter 2. In this chapter, we have investigated core-shell particles of two different effective volume fractions, $\phi_{eff} = 1.68$ and 1.21 at 15°C, and the corresponding particle



Figure 8.3: Relative viscosity η_{rel} (measured at 15°C) vs. particle concentration c in wt% for aqueous suspensions of core-shell particles. The solid line is a fit to equation 2.14.

concentrations in suspensions are listed in table 8.1.

We have systematically studied the temperature-dependent rheological behavior of dense aqueous suspensions of thermoresponsive core-shell particles of two effective volume fractions. We study the temperature-dependent viscoelastic properties of these suspensions by performing temperature sweep rheological experiments at a fixed oscillatory strain amplitude 0.5% and angular frequency 0.5rads⁻¹. Figure 8.4(a) shows a plot of the elastic and viscous moduli, G' and G'', as a function of temperature T for aqueous suspensions of core-shell particles of different effective volume fraction, $\phi_{eff} = 1.68$ and 1.21 at 15°C. Three-step changes in the viscoelastic moduli of these suspensions can be clearly seen. We observe that both G' and G''

<i>c wt</i> .%	$c_p wt.\%$	ϕ_{eff}
18	10.17	1.68
13	10.17	1.21

Table 8.1: Fitted value of the polymer concentration, c_p , inside each particle in the swollen state, core-shell concentrations, c, used, and the effective volume fractions, ϕ_{eff} , of the core-shell particles in aqueous suspension.



Figure 8.4: (a) Temperature-dependent elastic moduli G' (solid symbols) and viscous moduli G'' (hollow symbols), of aqueous suspensions of core-shell particles of different effective volume fraction, $\phi_{eff} = 1.68$ and 1.21, at 15°C. (b) The measure of relative suspension rigidity, G' - G'', vs. temperature T, for aqueous suspensions of core-shell particles of different ϕ_{eff} .

fractions, the elastic modulus, G', exceeds the viscous modulus, G'', at T < LCST of shell particles, indicating viscoelastic solid-like behavior at these temperatures due to the jamming of the swollen core-shell particles. With increase in temperature, both viscoelastic moduli decrease, which can be attributed to the reduction in size of these particles and and the accompanying decrease in effective volume fractions (as discussed for PNIPAM particles in chapter 6).

Interestingly, we observe a linear response in mechanical properties of dense suspensions of these particles between temperatures $\approx 20^{\circ}$ C and $\approx 40^{\circ}$ C. The observed linear behavior of dense suspensions of core-shell particles can be attributed to a competition between hydrophobic attractive interactions between the collapsed shell

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Figure 8.5: Elastic moduli, G' (solid symbol), and viscous moduli, G'' (hollow symbols), as a function of applied strain amplitude, γ , for aqueous suspensions of core-shell particles of ϕ_{eff} = (a) 1.68 and (b) 1.21 for different suspension temperatures.

particles and repulsive interactions between the swollen cores. We see that both G' and G'' exhibit minimum values near the LCST of core particles. On raising the temperature above the LCST of core particles, we note a monotonic increase in both the viscoelastic moduli (figure 8.4(a)). Figure 8.4(b) shows the plot of G' - G'', which reveals the relative rigidity of viscoelastic suspensions over the temperature range explored in this chapter. For both samples, we note a significant decrease in the rigidity up to a temperature near the LCST of the core particles. The increase in suspension viscoelastic moduli and rigidity at temperature above the LCST of core particles is due to the attractive nature of both core and shell particles at these temperatures. It has been reported in the literature [17] and also discussed in chapter 6 that interactions between thermoresponsive particles transform from repulsive to attractive across the LCST due to a temperature-dependent enhancement in the hydrophobic nature of the constituent particles.

Next, we perform oscillatory strain amplitude sweep rheological experiments at a fixed angular frequency $\omega = 0.5 \text{rads}^{-1}$ to study the linear and non-linear mechanical properties of dense aqueous suspensions of core-shell particles of different effective volume fractions. Figures 8.5(a-b) display strain amplitude sweep data for dense



Figure 8.6: Linear modulus, G'_l , vs. temperature T for aqueous PNIPAM suspensions of core-shell particles of different effective volume fractions.

aqueous suspensions of core-shell particles of effective volume fractions 1.68 and 1.21, respectively. We note that for both ϕ_{eff} , G' and G'' are independent of the applied strain amplitude for small strain amplitude values, while G' > G'' indicates viscoelastic solid-like behavior of the sample. With a further increase in applied strain amplitude, the suspensions start yielding, which is characterized by a monotonic decrease in the elastic modulus, G', at higher strains. The viscous modulus, G'', exhibits a peak before decreasing, which reveals the onset of a yielding process. At higher strain values, G'' eventually exceeds G', indicating a fluid-like mechanical response of the suspensions. Figure 8.6 shows the temperature-dependent linear moduli, G'_l , defined as the magnitude of G' at very low applied strain amplitudes, for aqueous suspensions of core-shell particles of different ϕ_{eff} . We see that G'_l in-

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Figure 8.7: Plots of normalized stress vs. normalized strain (Lissajous curves) at different applied strains for aqueous suspensions of core-shell particles of $\phi_{eff} = 1.68$ at temperatures (a) 5°C, (b) 20°C, (c) 25°C, (d) 35°C, (e) 45°C and (f) 55°C.

creases with increase in ϕ_{eff} at all the temperatures. We observe a non-monotonic change in G'_l with varying suspension temperature, which is in agreement with our temperature sweep data plotted in figure 8.4. Interestingly, we observe two-step yielding in dense aqueous suspensions of these particles at temperature above the LCST of core particles (for example, at 45°C for $\phi_{eff} = 1.68$ and at 45°C, 55°C for $\phi_{eff} = 1.21$ in figure 8.4(a-b)). This observation reveals that above the LCST, the suspensions possess characteristics of glasses/gels comprising hard attractive colloidal particles (as discussed in more detail in the context of aqueous suspensions of PNIPAM particles in chapter 6).

To study the non-linear rheological behavior of dense suspensions of thermoresponsive core-shell particles, we perform large amplitude oscillatory shear (LAOS) experiments. Figures 8.7(a-f) represent Lissajous curves for aqueous suspensions of core-shell particles of $\phi_{eff} = 1.68$ at different temperatures. In a Lissajous curve, normalized stress is plotted versus normalized strain at different strain values. Similarly, Lissajous curves for aqueous suspensions of core-shell particles of $\phi_{eff} = 1.21$ at different temperatures are plotted in figure 8.8(a-f). For all the samples, we observe elliptical shapes for the Lissajous curves at small applied strain values, revealing the



Figure 8.8: Plots of normalized stress vs. normalized strain (Lissajous curves) at different applied strains for aqueous suspensions of core-shell particles of $\phi_{eff} = 1.21$ at temperatures (a) 5°C, (b) 20°C, (c) 25°C, (d) 35°C, (e) 45°C and (f) 55°C.

linear viscoelastic behavior of these suspensions. The fluctuation in the Lissajous curves observed in figures 8.8(c-e) (blue curves) at smaller strain amplitude can be attributed to residual noise present in the system, which affects the measurement of elastic properties of the low viscosity materials at very small applied strains [18, 19]. With increasing applied strain values, we observe deviation in the Lissajous curves from elliptical shapes for all the samples, which indicates the onset in non-linear rheological behavior of these samples. The inverted sigmoidal shape of Lissajous curve observed in figure 8.7(d) indicates strong intracycle shear thinning behavior [20] of the sample. The observed rectangular shapes of the Lissajous curves at very high strain values reveal the plastic nature of the suspensions at these strains [20].

We quantify Lissajous curves by estimating the normalized area under the curves, which is a measure of the normalized energy dissipation in the system [18, 20, 21]. The normalized energy dissipation E_n can be estimated using the relation: $E_n = A/\sigma_{max}\gamma_{max}$, where A is the area enclosed by a Lissajous curve and σ_{max} is the peak stress at an applied strain γ_{max} . Figures 8.9(a-b) show the plots of E_n as a function of applied strains at different temperatures for aqueous suspensions of core-shell particles of $\phi_{eff} = 1.68$ and 1.21 respectively. We observe that for all the ϕ_{eff} , E_n



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Figure 8.9: Normalized energy dissipation $E_n vs$. applied strain amplitudes at different temperatures for suspensions of core-shell particles of $\phi_{eff} = (a) 1.68$ and (b) 1.21. Ratio $G'_L/G'_M vs$. applied strain amplitudes at different temperatures for suspensions of core-shell particles of $\phi_{eff} = (c) 1.68$ and (d) 1.21.

increases with increase in temperatures which reveals a reduction in the mechanical rigidities of the suspensions. Moreover, for all the samples, we note an increase in the normalized energy dissipation E_n with increase in the applied strains. This reveals the yielding behavior of the sample due to increase in applied deformation.

Finally, we have estimated the ratio G'_L/G'_M where G'_L is the large-strain modulus or secant modulus evaluated at the maximum imposed strain and G'_M is the minimum-strain modulus or tangent modulus at $\gamma = 0$ [18, 21]. It has been reported that the $G'_L/G'_M > 1$ corresponds to intracycle strain stiffening and $G'_L/G'_M = 1$ indicates linear elastic regimes [18, 21]. In contrast, $G'_L/G'_M < 1$ reveals intracycle strain softening nature of the material. In figures 8.9(c-d), we plot the ratios G'_L/G'_M for dense aqueous suspensions of core-shell particles versus applied strains at different suspensions temperatures for the two effective volume fractions studied in this chapter. In both the samples, we observe some points where $G'_L/G'_M > 1$, mostly at temperature below and near the LCST of the shell particles, which indicates the presence of intracycle strain stiffening behavior of suspensions under these conditions.

8.4 Conclusions

Thermoresponsive core-shell particles with shell made of N-n-propylacrylamide (PN-NPAM) having LCST value of 21°C and core made of poly(n-iso-propylmethacrylamide) (PNIPMAM) having LCST of 44°C are synthesized using a two step free radical precipitation polymerization method. Our NMR spectroscopy data confirms the presence of the amide group in the NNPAM monomer. Presence of a large LCST gap between the core and shell results in linear swelling behavior of these particles, which we investigate using dynamic light scattering (DLS). Our temperatures sweep oscillatory data reveals three-step changes in the viscoelastic moduli of these suspensions with varying environmental temperature. Interestingly, we note that even dense aqueous suspensions on core-shell particles exhibit linear responses in mechanical properties in the temperature range between the LCSTs of core and shell particles. The increase in viscoelastic moduli of these suspensions at a temperature above the LCST of the core particles is attributed to the presence of attractive interactions between the constituent particles due to enhanced hydrophobicity in the system. In strain amplitude sweep experiments, we observe two-step yielding at temperatures above the LCST of core particles, reminiscent of suspensions of hard attractive colloidal glasses/gels. Non-linear rheological properties of dense aqueous suspensions of core-shell particles at different temperatures are studied by performing large amplitude sweep experiments. The observed rectangular shape in the Lissajous plot at very high applied strain values reveals the plastic nature of the suspensions at these strains. We observe that the normalized energy dissipation in the suspensions increases with increase in suspension temperature and applied strain values. This can be attributed to the decrease in the mechanical rigidity of the sample due to yielding of the suspensions. Our G'_L/G'_M data display evidence of intracycle strain stiffening at low temperatures and high applied strains. Given the novel rheology of suspensions of core-shell particles, more detailed studies of these systems are warranted.

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Chapter 9

Effects of core stiffness on the rheological properties of aqueous suspensions of thermoresponsive core-shell particles

9.1 Introduction

Thermoresponsive colloidal particles (microgel) in aqueous suspensions exhibit reversible phase transition by responding to changes in the environmental temperature [1, 2]. The most widely studied thermoresponsive microgel is poly(*N*-isopropylaryl-amide) (PNIPAM) which shows a volume phase transition temperature or lower critical solution temperature (LCST), of $\approx 34^{\circ}$ C [3, 4]. The thermoresponsive and phase behaviors of aqueous suspensions of PNIPAM particles are discussed in detail in section 1.6 of chapter 1 and chapters 5-6. Their thermoresponsive properties and the deformability of these materials make them potential candidates for use in many applications such as bio-sensors [5] and drug delivery [6, 7]. These thermoresponsive particles have also been widely used as a model system to study the colloidal glass transition [8, 9]. As discussed in chapter 8, Zeiser *et al.* [10] have synthesized

a new class of thermoresponsive core-shell microgels using a combination of two different thermoresponsive polymers with distinct LCST values. In these core-shell particles, the shell is made of ploy(N-n-propylacrylamide) (NNPAM), with LCST of $\approx 21^{\circ}$ C and the core consists of poly(N-iso-propylmethacrylamide) (NIPMAM) having LCST of $\approx 44^{\circ}$ C. The large LCST gap between the core and shell produces extraordinary linear swelling in the temperature range between the LCSTs of the core and shell. The detailed structures of core and shell-forming polymers and their swelling properties are provided elsewhere [11–13] and also discussed in chapter 8.

It has been reported that the degree of swelling of thermoresponsive microgels depends on the solvent quality and cross-linking density [14, 15]. The stiffness of these microgels, such as PNIPAM can be altered by varying the concentrations of crosslinkers (N, N'-methylenebisacrylamide (MBA)) and surfactant (sodium dodecyl sulfate (SDS)) during the synthesis process [16–19]. The different phases exhibited by aqueous suspensions of PNIPAM particles [20, 21] are discussed in chapters 5 and 6. In chapter 6, we studied the temperature and stiffness-induced changes in the rheological properties and self-assemblies of these particles in aqueous suspensions. Zeiser *et al.* [10] reported that the mechanical property (stiffness) of core particles affects the strength of linear swelling of the core-shell particles discussed above. They observed increase in the slope of the plot of linear swelling of core-shell particles *vs.* temperature with increase in core stiffnesses.

In this chapter, we investigate the linear and non-linear rheological behaviors of dense aqueous suspensions of thermoresponsive core-shell particles by varying the stiffness of the core and suspension temperature. Core particles of different stiffnesses were synthesized by varying the crosslinker N,N'- methylenebisacrylamide (MBA) concentration during the synthesis process. The core-shell particles were synthesized using two-step free radical precipitation polymerization method. The thermoresponsivity of core and core-shell particles with different core stiffnesses were studied using dynamic light scattering (DLS). Scanning electron microscopy measurements were performed to visualize thermoresponsive core-shell particles directly. The LCSTs of these particles are estimated using differential scanning calorimetry (DSC) experiments. The linear viscoelastic properties of dense suspensions of these particles are studied in oscillatory rheology experiments. Finally, non-linear rheological properties of core-shell particles with different core stiffnesses and at different suspension temperatures in dense aqueous suspensions are studied by analyzing Lissajous curves.

9.2 Sample preparation and experimental techniques

The shell monomer of the core-shell particles (N-n-propylacrylamide (NNPAM)), $LCST = 21^{\circ}C$) is synthesized using Schotten-Baumann reaction described elsewhere [22]. Figure 8.1 of chapter 8 shows 1H nuclear magnetic resonance (NMR) spectroscopy data of NNPAM monomer where the peak shown by the arrow confirms the presence of the amide (NH) group. Thermoresponsive core-shell particles with a shell consisting of poly(N-n-propylacrylamide) (PNNPAM) and a core made of poly(n-iso-propylmethacrylamide) (PNIPMAM) polymers are synthesized using two-step free radical precipitation polymerization method. The synthesis procedure of shell monomer and core-shell particles is discussed in detail in section 2.2.3 of chapter 2. The synthesis conditions of core particles of different stiffnesses are tabulated in table 9.1. The stiffness of the core is quantified in terms of the parameter α_{core} , which is the ratio of the PNIPMAM particle radii under fully swollen (low-temperature) and fully collapsed (high temperature) states. In the synthesis of core-shell particles in 200 mL of Milli-Q water, 0.6 g of core particles, 2.08 mL of NNPAM monomer, 0.048 g of crosslinker (MBA), 0.128 g of surfactant (SDS) and 0.248 g of APS were used. Aqueous suspensions of core-shell particles were prepared by adding powder of these particles in Milli-Q water. The experimental techniques used in this chapter (SEM, DLS, DSC and rheology) are described in chapter 2.

suspensions of thermoresponsive core-shell particles							225	
NIPAM	MBA	APS	S DS	α_{core}	C _p	ϕ_{eff}	С	
(g)	(% of NIPMAM)	(g)	(<i>g</i>)	$(d_{fullswell}/d_{fullshrunk})$	(wt.%)		(wt.%	
4.16	5	0.248	0.128	≈2.57	5.25	1.5	7.87	

≈2.18

≈1.46

1.5

1.5

16.06

24.93

10.71

16.62

0.128

0.128

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0.248

0.248

Table 9.1: Synthesis conditions used for the preparation of latexes of PNIPMAM by the one-pot polymerization method and characterization of the swelling properties (stiffnesses) of the synthesized particles. All the latexes were prepared in 400 mL volume. α_{core} , c_{p} , ϕ_{eff} , c are the maximum swelling ratio of core particles, polymer concentration inside each core-shell particle, effective volume fraction and particle concentration in aqueous suspension, respectively, at temperature 15°C.



Figure 9.1: Scanning electron micrograph of core-shell particles in dry state with α_{core} = (a) 2.57 and (b) 1.46.

9.3 **Results and discussions**

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Figure 9.1 shows the SEM images of thermoresponsive core-shell particles having different core stiffnesses in dry form. Core and shell structures can be seen in figure 9.1(a-b). The SEM image of core-shell particles with core stiffness $\alpha_{core} = 2.18$ is shown in figure 8.2(a) of chapter 8. Dynamic light scattering (DLS) experiments were performed to quantify the thermoresponsive behavior of core and core-shell particles. The DLS setup and protocol for estimating sizes of colloidal particles are described in section 2.3 of chapter 2. We measured the hydrodynamic diameter of core (PNIPMAM) particles within a temperature range between 20° C to 60° C at



Figure 9.2: (a) Temperature-dependent swelling ratios, $\alpha_T = d_{T^\circ C}/d_{55^\circ C}$, where $d_{T^\circ C}$ and $d_{55^\circ C}$ are the average hydrodynamic diameters of PNIPMAM core particles at temperatures T and $55^\circ C$ respectively, synthesized with different crosslinker concentrations in dilute aqueous suspensions. (b) Temperature-dependent swelling behavior of core-shell particles with three different stffnesses of core (PNIPMAM) particles. Inset shows a plot of the slopes of the linear fits, shown by black lines in the main figure, as a function of crosslinker concentration of core particles.

intervals of 2°C. We characterized the swelling behavior of PNIPMAM particles by measuring their maximum swelling ratios, α_{core} , defined as $d_{20^{\circ}C}/d_{55^{\circ}C}$, where $d_{20^{\circ}C}$ and $d_{55^{\circ}C}$ are the average hydrodynamic diameters of the PNIPMAM particles at 20°C and 55°C where these particles are in fully swollen and fully shrunk/collapsed, respectively.

Figure 9.2(a) shows the temperature-dependent swelling ratios, $\alpha_T = d_{T^\circ C}/d_{55^\circ C}$, where d_T is the average hydrodynamic diameter of the particles at temperature T. As discussed in chapter 6 for the PNIPAM case, due to higher osmotic pressure, the polymer networks in PNIPMAM particles with low crosslinker concentration undergo rapid expansion upon incorporating water. We note from figure 9.2(a) that the volume phase transition of PNIPMAM particles at the LCST becomes more continuous with increase in crosslinker concentration. We synthesized PNIPMAM particles with maximum swelling ratios $\alpha_{core} = 2.57$, 2.18 and 1.46 by varying crosslinker concentrations from 5.0 to 20.0 % of the NIPMAM monomer mass. The values of α_{core} corresponding to three different concentrations of the crosslinker MBA are



Figure 9.3: Relative viscosity η_{rel} (measured at 15°C) vs. particle concentration c in wt% for aqueous suspensions of core-shell particles with three different core stiffnesses. The solid line is a fit to equation 2.14.

listed in table 9.1. Figure 9.2(b) shows the temperature-dependent swelling ratios of thermoresponsive core-shell particles with different core stiffnesses. The swelling behavior of core-shell particles is discussed in chapter 8. As also reported earlier, we note that changes in the core stiffnesses affect the swelling properties of coreshell particles (figure 9.2(b)). Linear swelling behavior of these particles can still be observed in core-shell particles with different core stiffnesses in the temperature range between 25°C and 40°C. In the inset of figure 9.2(b), we plot the slope, K, of the linear fit of the plot of the temperature-dependent swelling ratio of core-shell particles vs. different stiffnesses of core particles. We note that the slope of the linear fit increases with increase in crosslinker concentration or stiffnesses of core particles. This can be attributed to the enhanced mechanical properties of the core



Figure 9.4: (a) Heat flow as a function of temperature T for aqueous suspensions of PNIPMAM core particles of two different maximum swelling ratios α_{core} . (b) Heat flow as a function of temperature T for aqueous suspensions of core-shell particles with two different maximum swelling ratios of core particles.

particles which affect the swelling behavior of the core-shell particles [10].

As discussed in earlier chapters (5-8), we use a modified parameter called effective volume fraction, ϕ_{eff} , to quantify the packing of soft and deformable thermoresponsive core-shell particles in dense aqueous suspensions. In figure 9.3, we plot the relative viscosity of aqueous suspensions of core-shell particles with different core stiffnesses as a function of particle concentration. The protocol of estimating ϕ_{eff} of soft deformable microgel particles using figure 9.3 is discussed in section 2.4.1a(i) of chapter 2. The concentrations of ingredients, chosen to ensure an identical effective volume fraction of core-shell particles $\phi_{eff} = 1.5$ at $T = 15^{\circ}$ C with different core stiffnesses, are listed in table 9.1.

The heat flows evaluated in the DSC experiments (the details are described in section 2.7 of chapter 2) for aqueous suspensions of PNIPMAM core particles of two different α_{core} are plotted in figure 9.4(a) as a function of temperature T. The temperatures corresponding to the endothermic peaks are characterized as the LCSTs of the PNIPMAM particles in an aqueous suspension. Figure 9.4(b) show the heat flow of aqueous suspensions of core-shell particles of two different core stiffnesses



Figure 9.5: (a) Temperature-dependent elastic moduli G' (solid symbols) and viscous moduli G'' (hollow symbols), of aqueous suspensions of core-shell particles with different maximum swelling ratios of core particles. (b) The measure of relative suspension rigidity, G' - G'', vs. temperature T, for aqueous suspensions of core-shell particles of different α_{core} .

vs. suspension temperature. The two endothermic peaks observed in figure 9.4(b) can be attributed to the phase transition temperatures (LCSTs) of core and shell particles. We note from figures 9.4(a) that the LCST of only the independent core particles in aqueous suspension occurs around 44° C. In contrast, the transition temperature corresponding to core particles in core-shell structure appears around 40° C (figure 9.4(b)). Clearly, the swelling properties of core particles get affected in the core-shell structure.

We investigated the temperature-dependent rheological behavior of dense aqueous suspensions of core-shell particles with three different core stiffnesses. We perform temperature sweep rheological experiments at a fixed oscillatory strain amplitude 0.5% and angular frequency 0.5 rads⁻¹. Figure 9.5(a) shows the plot of viscoelastic moduli (G' and G'') as a function of temperature T for aqueous suspensions of coreshell particles having three different core stiffnesses ($\alpha_{core} = 1.46, 2.18$ and 2.57) and at effective volume fraction, $\phi_{eff} = 1.5$ at 15°C. We note that, below the LCST of shell particles, both G' and G'' increase with increase in the stiffness of the core. This is in agreement with previous work on PNIPAM microgels [4], also reported in section 6.3.1 of chapter 6. Hence, the stiffness of the core affects the mechanical properties of core-shell particles. Since stiff core particles swell less than soft particles in aqueous suspension, we used a larger concentration of the core-shell particles to get the same effective volume fraction at 15°C (table 9.1). This explains the increase in G' and G'' of suspensions of core-shell particles with increase in the stiffness of the core. For all the samples, the elastic modulus, G', exceeds the viscous modulus, G'', at T < LCST of the shell, which indicates viscoelastic solid-like behavior at these temperatures due to jamming of the swollen core-shell particles. We also note a collapse of the moduli at the LCST of the shell due to a sharp reduction in the size of the constituent particles (figures 9.5(a-b)). The more rapid collapse in the viscoelastic moduli of dense suspensions of core-shell particles with a soft core at the LCST can be attributed to enhanced compression of the soft core by the shell as also observed in figure 9.2(b). Both viscoelastic moduli exhibit minima at the LCST of the core. We observe a linear decrease in the moduli of core-shell particle suspensions when the core stiffness is high. For the core-shell particles with the softest cores, the suspension show liquid-like behavior. On further raising the temperature beyond the LCST of the core, we note a gradual increase in the viscoelastic moduli, with G' eventually exceeding G'' for all the suspensions. Figure 9.5(b) displays plots of G' - G'', which is a measure of the relative rigidity of the viscoelastic suspensions over the range of temperatures explored in this chapter. We note a significant loss of rigidity near the LCST of shell particles for all the samples. Interestingly, we note that G'' > G' near the LCST of shell for only the suspension of the softest core ($\alpha_{core} = 2.57$, indicated by the red ellipse in figure 9.5(b), revealing viscoelastic liquid-like behavior of the suspensions. The observed increase in suspension viscoelastic moduli (figure 9.5(a)) and rigidity in figure 9.5(b)at a temperature above the LCST of core particles can be attributed to the attractive nature of both core and shell at these temperatures. It has been reported in the literature [3] and also discussed in chapters 6 and 8 that the interactions between thermoresponsive particles transform from repulsive to attractive across the LCST



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Figure 9.6: Elastic moduli, G' (solid symbol), and viscous moduli, G'' (hollow symbols), as a function of applied strain amplitude, γ , for aqueous suspensions core-shell particles having $\alpha_{core} =$ (a) 1.46, (b) 2.18 and (c) 2.57 at different suspension temperatures. (d) Linear modulus, G'_l , vs. temperature T for aqueous PNIPAM suspensions of core-shell particles with different core stiffnesses.

due to increase in the hydrophobic nature of constituent particles.

Next, we perform oscillatory strain amplitude sweep rheological experiments at a fixed angular frequency $\omega = 0.5 \text{rads}^{-1}$ to study the linear and non-linear mechanical properties of dense aqueous suspensions of core-shell particles of different core stiffnesses. Figure 9.6(a-c) shows strain amplitude sweep data for dense aqueous suspensions core-shell particles with $\alpha_{core} = 1.46$, 2.18 and 2.57, respectively. We note that for all suspensions, both viscoelastic moduli, G' and G'', are independent



Figure 9.7: Plots of normalized stress vs. normalized strain (Lissajous curve) at different applied strains for aqueous suspensions of core shell particles with $\alpha_{core} = 1.46$ at temperatures (a) 5°C, (b) 20°C, (c) 25°C, (d) 35°C, (e) 45°C and (f) 55°C.

of the applied strain amplitude at small values with G' > G'', indicating viscoelastic solid-like behavior of the sample. With a further increase in the applied strain amplitude, the sample starts yielding, which is characterized by a monotonic decrease in the elastic modulus, G', at higher strains. The viscous modulus, G'', at temperatures below the LCST of shell particles, shows a peak before decreasing, which reveals the onset of a yielding process. At higher strain values, G'' exceeds G', indicating viscoelastic liquid-like behavior of the suspensions. Figure 9.6(d) represents temperature-dependent linear moduli, G'_{l} , defined as the magnitude of G'at very low applied strain amplitudes for aqueous suspensions of core-shell particles of different core-stiffnesses. We see that G'_{l} increases with increase in stiffness of core particles at all the temperatures and exhibits non-monotonic change with varying suspension temperature. These results are in agreement with our temperature sweep data shown in figure 9.5. Interestingly, we observe two-step yielding in dense aqueous suspensions of core-shell particles at a temperature above the LCST of the core particles. Such two-step yielding is not observed for the suspensions of particles having higher core stiffnesses at 55°C. As discussed in more detail in chapter 6, demonstrates the characteristics of glasses/gels made of hard, attractive colloidal particles. [23].

Chapter 9. Effects of core stiffness on the rheological properties of aqueous suspensions of thermoresponsive core-shell particles



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Figure 9.8: Plots of normalized stress vs. normalized strain (Lissajous curves) at different applied strains for aqueous suspensions of core shell particles with $\alpha_{core} = 2.18$ at temperatures (a) 5°C, (b) 20°C, (c) 25°C, (d) 35°C, (e) 45°C and (f) 55°C.

We study the non-linear rheological behavior of dense suspensions of thermoresponsive core-shell particles with different core stiffnesses by performing large amplitude oscillatory shear (LAOS) experiments. Figures 9.7(a-f) show Lissajous curves for aqueous suspensions of core-shell particles with $\alpha_{core} = 1.46$ at different suspension temperatures. In Lissajous curve, we plot the normalized stress as a function of normalized strain at different strain values (figures 9.7(a-f)). Similarly, Lissajous curves for aqueous suspensions of core-shell particles with $\alpha_{core} = 2.18$ and 2.57 at different temperatures are plotted in figures 9.8(a-f) and 9.9(a-f), respectively. For all the suspensions, we note elliptical shapes of Lissajous curves at smaller applied strain values which reveal the linear viscoelastic behavior of these suspensions (blue curves in figures 9.7(a-f), 9.8(a-f) and 9.9(a)). The fluctuations in the Lissajous curves observed in figures 9.7(d), 9.8(d) and 9.9 (blue curves) at smaller strain amplitudes can be attributed to residual noise present in the system, which influence the elastic properties of the low viscosity materials at very small applied strains [24, 25]. With increase in the applied strain values, we note deviation from the elliptical shape in Lissajous curves for all the samples, which is the characteristic of the onset of non-linear rheological behavior of these samples. The inverted sigmoidal shapes of Lissajous curves for large strains show strong intracycle shear thinning behavior



Figure 9.9: Plots of normalized stress vs. normalized strain (Lissajous curves) at different applied strains for aqueous suspensions of core shell particles with $\alpha_{core} = 2.57$ at temperatures (a) 5°C, (b) 20°C, (c) 25°C, (d) 35°C, (e) 45°C and (f) 55°C.

of the sample [23]. The observed rectangular shape in Lissajous curve at very high strain values suggests the plastic nature of the samples at these strains.

We analyze the Lissajous curves by estimating the normalized area enclosed by each Lissajous curve, which is the measure of normalized energy dissipation in the system [23, 24, 26]. We can estimate the normalized energy dissipation E_n using the relation: $E_n = A/\sigma_{max}\gamma_{max}$, where A is the area enclosed by an Lissajous curve and σ_{max} is the peak stress at an applied strain γ_{max} . Figures 9.10(a-c) show the plot of E_n as a function of applied strains at different temperatures for aqueous suspensions of core-shell particles with $\alpha_{core} = 1.46$, 2.18 and 2.57, respectively. We note that for all the suspensions, E_n increases with increase in temperatures and applied strains. As expected, this implies a reduction in the mechanical rigididty of the suspensions with increasing temperature and applied deformation.

Finally, we have calculated the ratio G'_L/G'_M where G'_L is the large-strain modulus or secant modulus evaluated at the maximum imposed strain and G'_M is the minimum-strain modulus or tangent modulus at $\gamma = 0$ [24, 26]. It has been previously reported that the ratio $G'_L/G'_M > 1$ corresponds to intracycle strain stiffening





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Figure 9.10: Normalized energy dissipation $E_n vs.$ applied strain amplitudes at different temperatures for suspensions of core-shell particles with $\alpha_{core} = (a) 1.46$, (b) 2.18 and (c) 2.57. Ratio $G'_L/G'_L vs.$ applied strain amplitudes at different temperatures for suspensions of core-shell particles having $\alpha_{core} = (d) 1.46$, (e) 2.18 and (f) 2.57.

and $G'_L/G'_M = 1$ indicates the linear elastic regime [24, 26]. On the other hand, the ratio $G'_L/G'_M < 1$ corresponds to the intracycle strain softening nature of the sample. In figures 9.10(d-f), we plot the ratios G'_L/G'_M for dense aqueous suspensions of core-shell particles as a function of applied strain at different suspensions temperatures for different stiffnesses of core particles. In all the suspensions, we observe some points where $G'_L/G'_M > 1$, mainly at temperatures below and near the LCST of shell particles, which indicates intracycle strain stiffening of these suspensions under these conditions [24, 26]. Similar results were also reported in chapter 8.

9.4 Conclusions

In this chapter, we have investigated the linear and non-linear rheological properties of thermoresponsive core-shell particles, having a shell constituted by N-npropylacrylamide (PNNPAM) having LCST value of 21°C and core made of poly(niso-propylmethacrylam-ide) (PNIPMAM) having LCST of 44°C, while varying the stiffnesses of core particles and keeping the shell composition fixed. We synthesized core (PNIPMAM) particles of different stiffnesses by varying the crosslinker concentration in a free radical precipitation polymerization method. We quantify the stiffness of PNIPMAM particles by estimating their maximum swelling ratios. For all the samples, our temperature sweep oscillatory rheological data yield three-step changes in the viscoelastic moduli with varying the suspension temperature. We observed that at identical effective volume fractions, both viscoelastic moduli of aqueous suspensions of core-shell particles increase with increase in the core stiffnesses. This can be attributed to enhancement in the mechanical properties of core particles and the concentration of core-shell particles in suspensions. We note that dense aqueous suspensions of core-shell particles with relatively stiffer cores exhibit linearly varying mechanical properties with temperature between the LCST of core and shell particles. The observed increase in mechanical strength of these suspensions at temperatures above the LCST of the core particles is attributed to the presence of attractive interactions between the constituent particles due to enhanced hydrophobicity in the system. In strain amplitude sweep experiments, we observed two-step yielding at temperatures above the LCST of the core particles which is reminiscent of suspensions of hard attractive colloidal glasses/gels. Non-linear rheological behavior of dense aqueous suspensions of core-shell particles at different temperatures and core stiffnesses are studied by performing large amplitude sweep experiments. We noted rectangular shapes in the Lissajous plot at very high applied strain values, which indicate the plastic nature of the suspensions at these strains. We observed that for all the samples, the normalized energy dissipation increases with increase in suspension temperature and applied strain values. This is because of a decrease in the mechanical rigidity of the sample due to an increase in temperature and onset of suspension yielding. We see evidence of intracycle strain stiffening at higher strains and low temperatures.

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Chapter 10

Summary and future directions

This chapter summarizes the main results of this thesis and discusses the scope for future work. The main focus of this thesis is to study the jamming dynamics, rheological behavior, length scale-dependent rheology and self-assemblies of colloidal particles in aqueous suspensions using different experimental techniques. Aqueous suspensions of Laponite clay particles, which exhibit properties of physical aging, and two types of thermoresponsive microgels (poly(N-isopropylacrylamide)) or PNI-PAM, and thermoresponsive core-shell particles) are the model systems investigated in this thesis. The aging dynamics of aqueous Laponite suspensions were studied mainly using dynamic light scattering and rheological experimental techniques. Dynamic light scattering measurements were employed to study the thermoresponsive behaviors of microgel systems. These particles were synthesized using free radical precipitation polymerization methods and directly visualized with a scanning electron microscope (SEM). Various bulk rheological properties of dense suspensions of colloidal particles, such as aging, linear and non-linear viscoelasticity, yielding and stress relaxation, were investigated using a rheometer. Rheo-dielectric spectroscopy was employed to study the dynamics of aqueous PNIPAM suspensions at very different length scales. The microstructures of colloidal particles in dense suspensions were studied using cryogenic scanning electron microscopy (cryo-SEM).

Chapter 1 briefly described the background information required for understanding the experimental results presented in this thesis. The properties of colloidal particles and interactions between them in aqueous suspensions were discussed in the context of hard, soft and charged colloidal systems. The different phases formed by colloidal systems and their glass transition dynamics were reviewed. Next, the aging dynamics of aqueous suspensions of Laponite platelets and their phase diagram were discussed. Finally, we reported the thermoresponsive behavior of microgel systems.

The different experimental techniques employed in this thesis were explained in chapter 2. The synthesis methods used to make thermoresponsive PNIPAM and core-shell particles were discussed. This chapter describes the dynamic light scattering (DLS) setup and protocol for estimating the sizes of colloidal particles using DLS. Next, rheometry and different types of rheological experiments that were performed to study the bulk properties of colloidal particles in suspensions were discussed. Rheo-dielectric spectroscopy was also introduced, which allowed us to study the material's properties over a length scale range over varying several (7–8) orders of magnitude. Finally, imaging techniques SEM and cryo-SEM and differential scanning calorimetry (DSC) were briefly described.

In chapters 3 and 4, we studied the effects of solvent (water) structure and electrostatic interactions on the physicochemical properties of aqueous suspensions of Laponite clay particles. In chapter 3, we achieved control over the inter-molecular hydrogen bonds of the liquid water suspension medium by adding kosmotropic (structure-inducing) and chaotropic (structure-disrupting) molecules. A more structured medium, achieved by adding non-dissociating kosmotropic molecules, accelerated the aging dynamics of Laponite suspensions by enhancing osmotic pressure gradients in the colloidal suspensions. In contrast, the addition of chaotropic molecules induced opposite effects. The presence of uncharged, non-dissociating molecules in the suspension medium was seen to significantly alter the aging dynamics of colloidal suspensions. In the presence of dissociating ions that can modify the water structure, we consistently observed that electrostatic inter-particle interactions dominate over suspension medium structure in determining the physicochemical properties of the colloidal suspensions.

In chapter 4, we further verified our hypothesis that electrostatic interactions dominate over suspension medium structure in the presence of dissociating ions. We devised a new temperature-controlled experimental protocol. We first disrupted the hydrogen bonds in the medium by raising its temperature to a pre-determined value before suspending Laponite particles; we referred to this as prefixed temperature experiments. Interestingly, we observed faster aging compared to a Laponite suspension that was heated after preparation (postfixed temperature experiments) at room temperature. Heating accelerates the dissociation of sodium ions present in the intra-gallery spaces of the Laponite layers and results in strong inter-colloid electrostatic interactions. We verified that the dissociation of ions is faster in the prefixed experiments and concluded that electrostatics dominate over changes in suspension medium structure in determining the aging dynamics of aqueous colloidal suspensions at different temperatures. Since clay is the main ingredient of soil, the physicochemical properties of its aqueous suspensions are expected to strongly affect large-scale geological phenomena such as landslides, river delta formation and liquefaction of quicksand. The results reported in chapters 3 and 4 should play a significant role in advancing the existing knowledge on structural stability and soil dynamics. These results are sufficiently general and can be extended to any aging colloidal suspension where osmotic pressure gradients and electrostatic interactions determine the physicochemical properties of the system.

In chapters 5 and 6, we studied the thermoresponsivity, rheological behavior and self-assemblies of dense aqueous suspensions of poly(N-isopropylacrylamide) (PNI-PAM) particles synthesized by varying surfactant (chapter 5) and crosslinker concentrations (chapter 6) in a free radical precipitation polymerization method. PNIPAM particles of different sizes were synthesized by varying surfactant (sodium dodecyl sulfate (SDS)) concentrations. Increasing SDS concentration produces PNIPAM particles of smaller sizes. We showed that PNIPAM particles of different stiffnesses can be synthesized by varying concentrations of SDS and crosslinker (N, N)N'-methylenebisacrylamide (MBA)) during the synthesis process. We quantified the stiffnesses of these particles by measuring their maximum swelling ratios, α . The stiffness of PNIPAM particles increases with increasing MBA concentration or decreasing SDS concentration. In chapter 5, changes in the particle stiffness with changing size were attributed to the different crosslink densities (CLDs) of the particles. A statistical model for the Helmholtz free energies of the microgel was used to estimate the CLDs of PNIPAM particles in aqueous suspensions, which were observed to increase with increasing particle stiffness. When temperature was increased, soft particles deswelled more quickly than stiff particles because they are characterized by higher osmotic pressures. The mechanical moduli of dense aqueous suspensions of PNIPAM particles of identical packing fractions were seen to increase with increase in the stiffnesses of individual particles. For all the samples studied in these chapters, a non-monotonic increase in the suspension viscoelasticity was observed with increase in suspension temperature across the lower critical solution temperature (LCST).

The key finding reported in chapter 6 is that suspensions containing the softest PNIPAM particles undergo a gel-liquid-gel transition as temperature increases, with a significantly weaker gel phase above the LCST. In contrast, PNIPAM microgel suspensions with high particle stiffness form disordered glassy phases below and above the LCST while retaining a finite but low rigidity at the LCST. With increasing temperature, PNIPAM particles become more hydrophobic, and the interparticle interaction in aqueous suspension shifts from repulsive to attractive, which causes a rise in suspension rigidity above LCST. The suspension microstructures visualized using cryo-SEM imaging showed significant changes in particle self-assemblies,

thereby verifying our rheological results. Suspensions of soft PNIPAM particles formed gel-like networks at temperatures below and above the LCST. On the other hand, suspensions comprising the stiff PNIPAM particles remained in a glassy state at all the experimental temperatures studied in this work. Using thermoreversible microgel suspensions, we reported for the first time that particle stiffness influences phase transformations. The analysis of Lissajous curves will enable the study of the non-linear rheological behavior of PNIPAM suspensions of different stiffnesses and temperatures in the future.

Chapter 7 reported the use of dielectric spectroscopy to probe the the dynamics of PNIPAM particles at very different length scales under large applied deformation. We performed rheo-dielectric experiments to study the dielectric response of PNIPAM colloidal suspensions under large applied deformations for different particle effective volume fractions and solvent temperatures. We analyzed the real and imaginary parts of the dielectric permittivities of aqueous PNIPAM suspensions of different effective volume fractions, subjected to large applied strain amplitudes, at temperatures below, near and above the LCST over a wide frequency range of the applied electric fields. For all the samples investigated in this chapter, the real parts of the dielectric permittivities displayed two distinct dielectric relaxation processes in the low and high-frequency regimes. While both real and imaginary contributions of the dielectric permittivities of densely-packed aqueous PNIPAM suspensions decrease with increase in strain amplitudes below the LCST, we reported a counterintuitive slowing down of dielectric relaxation processes in both relaxation regimes.

Interestingly, we also observed a simultaneous speeding up of the bulk stress relaxation dynamics of these PNIPAM suspensions in bulk rheological measurements. Therefore, while our dielectric relaxation data indicated dynamical slowing down at the shortest accessible length scales, our bulk rheological data pointed to simultaneous shear thinning rheology at macroscopic length scales. We attributed the observed length scale-dependent response functions to the shear-induced rupture of fragile clusters of swollen PNIPAM particles in densely-packed suspensions below the LCST. We proposed that while the restricted motion of the entangled PNIPAM chains under shear increases the dielectric relaxation time, the shear-induced disruption of the swollen PNIPAM microstructures accelerates the stress relaxation in the bulk. To the best of our knowledge, rheo-dielectric analysis has never been used to examine dense colloidal microgel suspensions. However, it has been used to study nematic liquid crystals, polymers, electrorheological fluids (ERFs), conducting carbon black suspensions, viscoplastic droplets, and elastomers. As discussed in chapter 6, PNIPAM particles of different stiffnesses can show a rich variety of rheological and phase behaviors. In the future, it will be interesting to study their dielectric responses under large applied deformations using rheo-dielectric spectroscopy. The rheo-dielectric responses of these suspensions by varying the frequency of the applied deformation can be an interesting issue to explore in future work. Since the rheo-dielectric technique remains quite underutilized in the study of soft materials, our rheo-dielectric setup can be used to study different colloidal systems such as shear thickening cornstarch suspensions, suspensions of aging Laponite particles, dense aqueous suspensions of polystyrene particles, etc. It can also be used to study the non-linear rheo-dielectric and electrorheological properties of soft glasses under large electric fields.

Linear and non-linear rheological behavior of dense aqueous suspensions of linear thermoresponsive core-shell particles were studied in chapters 8 and 9. Thermoresponsive core-shell particles with shells composed of poly(*N*-n-propylacrylamide) (PNNPAM) with LCST of 21°C and core comprising poly(n-iso-propylmethacrylamide) (PNIPMAM) having LCST of 44°C were synthesized using a two-step free radical precipitation polymerization method. NMR spectroscopy data confirmed the presence of the amide group in the shell monomer (NNPAM), which was synthesized using Schotten–Baumann reaction. A gap of 23°C between the LCSTs of the core and shell-forming polymers produces the observed linear swelling property. Changes in the stiffnesses of the core particles affect the swelling behavior of the synthesized core-shell particles. The viscoelastic moduli of dense aqueous suspensions of core-shell particles were reported to increase with increasing effective volume fraction (ϕ_{eff}) or with increasing core stiffnesses at an identical ϕ_{eff} .

Interestingly, the mechanical behavior of dense suspensions of core-shell particles also exhibited linear response when temperatures was increased between the LCSTs of core and shell particles. The viscoelastic moduli and rigidity of aqueous suspensions of core-shell particles increased with temperature above the LCST of the core particles. This is attributed to the transformation of interparticle interactions from repulsive to attractive across the LCST. Suspensions of core-shell particles with the softest cores exhibited liquid-like behavior near the LCST of the shell particles. In contrast, core-shell particles with relatively stiffer cores exhibited low but finite rigidity at the same temperature. The non-linear rheological behavior of these suspensions was studied by performing large amplitude oscillatory strain experiments. At very high applied strain values, we observed rectangular shapes in the Lissajous plots, indicating the emergence of plasticity in the suspensions. The normalized energy dissipation of all samples was seen to increase with increasing suspension temperature and applied strain. This was attributed to a decrease in the mechanical rigidity of the samples due to increase in temperature and yielding of the suspensions. Future studies can examine the glass transition dynamics of core-shell particles in aqueous suspensions and their relationship with core stiffnesses in more detail. Contributions from higher harmonics in the non-linear rheological behavior of core-shell particles under non-linear applied perturbations will also serve to enhance our understanding of these interesting materials.

Given that colloidal suspensions are ubiquitous in the industry and have been exploited as functional and adaptive materials, careful studies of their structures, dynamics, rheology, stability and phase behaviors are of utmost importance. To summarize, this thesis presented a detailed study of the physical properties of a subset of these very important materials.

Thesis report responses

We thank both the referees for the careful reading of the thesis and their insightful comments and suggestions.

Response to referee 1

Chapter 3-

1. I am curious to know how the candidate has decided on the concentration of the additives used. For example, in Fig 3.4, DMF and glucose have different concentrations. Fig 3.5 (f) is a critical result that collapses the data of all concentrations on a master curve. The discussion of this data is not satisfactory in this chapter. Please explain significance of this master curve in some details.

Reply – In chapter 3, we study the effects of a wide range of additives on aqueous Laponite suspensions. We have divided the additives into two categories (dissociating and nondissociating) and have included quantitative comparisons of the effect of each additive on the aging dynamics of Laponite suspensions. We have reported that the aging dynamics of Laponite suspensions in presence of non-dissociating molecules such as glucose and DMF are governed by the osmotic pressure gradients that arise due to structural changes in water induced by these additives. On the other hand, electrostatic interactions dominate over any changes in solvent microstructure in the presence of NaCl and KCl. Since hydrogen bonding is substantially weaker than electrostatic interactions, a significantly larger quantity of glucose and DMF additives are required to achieve comparable changes in the microscopic dynamics and bulk rheology as the additives NaCl and KCl. We have therefore chosen additive concentrations such that their incorporation ensures a significant change in the aging dynamics of Laponite suspensions.

The excellent superpositions of the relaxation time data shown in Fig 3.5 (f) suggest that the temporal evolutions of the relaxation processes in all the Laponite suspensions are self-similar when various additives are introduced in the sample, indicating that the underlying energy landscapes also remain self-similar in the presence of these additives. Therefore, while the rate of the aging process is altered by incorporating additives, the underlying dynamical mechanisms such as the swelling of clay clusters and the exfoliation of single particles continue to happen, though at different rates that are determined by the nature of additives as explained earlier and in sections 3.3.1 and 3.3.2 of chapter 3.

 Fig 3.14 – This graph contains data for all the additives. If I compare moduli in the linear viscoelastic regime, there are differences in additive concentration and type of the additive. The candidate has drawn conclusions based on the nature of the additives, and I would also like the candidate to comment on the effect of concentration. Reply – Concentrations of the additives are chosen so as to ensure significant changes in the aging dynamics of the Laponite suspensions. The key result of this study is that the dissociating or non-dissociating nature of the additive determines the aging behaviour. While for dissociating additives, the sample aging is determined by the evolution of interparticle interactions, non-dissociating additives alter the population and strength of hydrogen bonds in the suspension medium, which, in turn, alter the aging behaviour. The logic behind the selection of additive concentrations and the discussion on the reasons behind the choices made have been clarified in the response to the previous question of the referee.

3. Are NaCl and KCl the only ionic additives? Can the candidate hypothesize what would be the effect of, say, other multivalent electrolytes?

Reply – For the divalent additive MgCl₂, Mg²⁺ ions are expected to participate in the Debye layer and give rise to similar effects as K⁺ and Na⁺ ions in aqueous Laponite suspensions. Incorporation of ions regardless of their valency should result in enhanced aging dynamics due to the modification of electrostatic interparticle interactions. Indeed, Camille et al. (Rheologica Acta (2022) **61**, 811–825) have reported that at low MgCl₂ concentrations, aqueous suspensions of a mixture of Laponite and Bentonite clay form a stronger gel. In a recent study, Mohammed et al. (Materials, 2023, **16**, 101) have used X-ray photon correlation spectroscopy experiments to investigate the relaxation behaviour of aqueous Laponite suspensions in the presence of CaCl₂, MgCl₂ and CsCl. They have reported accelerated aging dynamics of Laponite suspensions in the presence of salts of higher valencies. We therefore believe that while the qualitative features of the present data would remain invariant, adding multivalent ionic salts would have accelerated the aging process by further slowing down the particle dynamics.

Chapter 4- This chapter discusses the effect of thermal histories on the aging dynamics of Laponite. Fig. 4.4 (b) are there any error bars on this data set? The candidate



cla Figure R1. Yield stresses (σ_y) of Laponite suspensions at age $t_w = 200$ minutes for temperatures in the range 15-55°C both for prefixed and postfixed temperature experiments.

Reply- The G'₁ data in Fig 4.4(b) of the thesis are obtained from linear fits to the linear viscoelastic (LVE) region of the strain amplitude sweep data shown in Fig. 4.4 (a). Since the variation of G' in the LVE region is minimal, the error bars obtained from linear fits to the G' -strain amplitude data to obtain G'_1 are not significant.

1. Yield stresses are not different; please explain

Reply – Yield stresses σ_y vary in the range between 0.002 and 24.9 Pa. for prefixed experiments and 0.018 and 10.7 Pa. for postfixed experiments. We would like to point out that the data shown in Fig. 4.4(b) are plotted on log scale. In Fig. R1, we plot the data on a linear-linear scale to amplify the changes in yield stress with temperature.

Chapter 5- This is well written chapter. It nicely relates the swelling ratios to crosslinking densities and the size of the particles. I am curious to know if the candidate has considered the polydispersity of the synthesize particles.

Reply- In this thesis, we have not varied the polydispersity of the PNIPAM particles. We have used a one-pot synthesis method which produces nearly monodisperse particles (polydispersity ~ 10%). However, my other lab members have varied the polydispersity of PNIPAM particles using semi-batch synthesis protocol and have studied the jamming dynamics of dense suspensions constituted by polydisperse PNIPAM particles.

Chapter 6 –

This comprehensive chapter relates PNIPAM stiffness to even particle hydrophobicity.

1. Fig. 6.10 for samples with swelling degree with alpha = 2 or 3, the earlier data showed that they are viscoelastic liquids with G' $\sim 10^{-1}$ Pa. Is it possible to measure the yield stress of these samples accurately, as reported in Fig. 6.10(b)?

Reply – We have used the protocol suggested by Laurati *et al.* (Journal of Rheology, **55**, 637-706 (2011)) to compute yield stresses of all the materials investigated. Representative data showing characterisation of yielding behaviours of the samples studied by us are shown in Figs. 2.8 and 3.8. Using this recipe, we have calculated yield stresses or strains plotted in Figs. 3.7e, 4.4b, and 6.10b. As shown in Fig. 6.9, these samples exhibit viscoelastic solid-like behaviour at very low applied strain amplitudes, which enables us to estimate the yield stresses by using Hookes law.

2. There is data reported for average pore size; perhaps the candidate can mention how any pores are analysed to arrive at the reported average.

Reply- We have estimated the area of each pore using the area detection algorithm available in ImageJ software (Java 1.8.0_172, developed by Wayne Rasband, NIH, US). Next, we have averaged individual pore area estimates over ~ 500 pores, which we achieved by carefully analysing 4-5 cryo-SEM images.

Chapters 8 and 9 – Report promising results of some of experiments with core-shell particles. Apart from the structure, I am curious to know about the candidates hypothesis: how would the rheological response differ from the solid PNIPAM particles? Can one change the swelling ratio/sizes by a different mechanism than what is already reported in earlier chapters? Nonetheless, these are exciting results.

Reply – The difference in the rheological behaviours of core-shell (PNIPMAM-PNNPAM) and PNIPAM particles is mainly due to structural differences in these particles. Synthesizing PNIPAM particles in a different ionic liquid or changing the nature of the crosslinker can be possible routes to achieve control over the swelling properties of these particles.

Response to referee 2

1. P10

The boundaries between jammed and unjammed states is entirely system dependent. The jamming phase diagram therefore unifies the kinetic arrest phenomenon seen in different materials. If the boundaries are system dependent, how can diagram unify for deferent materials?

Reply- Fig. 1.3a of the thesis is a speculative representation of the basic mechanisms driving the jamming-unjamming transition in a wide range of nonequilibrium systems. All jammed systems share qualitative features that can therefore be described by plotting a single phase diagram. The jamming phase diagram (Fig. 1.3a) conveys that any jammed system can be unjammed by raising the temperature, decreasing the particle volume fraction or by applying stress. The phase boundaries change depending on the material properties, for example with changing interparticle attractive interactions (Fig. 1.3b and ref 52 in chapter 1). The phase diagram captures a subset of the different routes by which a kinetically arrested system may be fluidised. It is therefore purely representative of some general fundamental principles, but does not capture the exact details of jamming-unjamming phenomena.

2. There is no mention of rate effect (how fast the temperature is changed or volume fraction is changed) in leading to arrested states, though this has been already pointed out in Fig. 1.2. Therefore, last statement related to physical aging is not surprising. However, both the figures do not incorporate "field induced" effect. Therefore, it is expected that they will not describe shear induced (or other external field induced) transformations.

Isn't all of this related to the use of "phase diagram" for non-equilibrium system?

Reply- We agree with the referee that the non-equilibrium phase diagrams plotted in Figs. 1.2 and 1.3 do not account for the rate of changes in the parameters that drive the system into a jammed state. As mentioned in section 1.4, the above mentioned phase diagrams fail to explain the shear-induced jamming transition driven by the physical aging process. As also mentioned in the earlier response, this speculative phase diagram fails to consider several key details that should be required for a complete description of the jamming-unjamming transition.

Fig. 2.8 – How justified is the use of Hooks law to characterize peak stress vs. peak strain data? At each data point – stress vs strain data is cyclic and non-linear given viscoelasticity.
Pre-yield, the material is supposed to be elastic – storing energy. Clearly, all along the green straight line in this figure, there is dissipation in the material.

How convencing it is to notice that G'' is an order of magnitude below, therefore dissipation can be ignored. (this is definitely not the case for all materials though, for example in Fig 3.7 – some compositions show G' and G'' of the same order)

Isn't it more appropriate to identify this point as one of measure of departure from linear viscoelasticity?

Reply- The referee is correct. We have used this protocol since the viscous modulus in our system is lower than storage modulus by about an order of magnitude at least in most experiments. This treatment, which we follow as suggested by Laurati *et al.* (Journal of Rheology, **55**, 637-706 (2011)), is based on recording the point of departure from Hooke's law, and allows us to come up with fairly accurate estimates of yield strain with varying control parameters as described later (Figs. 3.7e, 4.4b, and 6.10b of the thesis).

4. Fig. 3.9 – Though a comment has been made about the soft glassy nature of results, would it be worthwhile to look at signature/transitions of cage-breaking etc from LAOS data? Would this analysis along with DLS provide more insights?

Does \tau_1 correlates with tan \delta at low strains?

Reply- Study of LAOS data, such as analysis of Lissajous plots, is an excellent tool to understand the rheological behaviour of materials in their non-linear regimes. However, in this chapter, our main focus was to understand the effect of changes in microstructures and linear viscoelasticity due to incorporation of different additives on the aging dynamics of aqueous Laponite suspensions. The study of nonlinear rheology would definitely be an interesting direction to follow in future attempts to understand the material in greater detail across a broader range of control parameters.

The tau_1 is the time scale related to the diffusion on particles in the cages formed by their neighbour. On the other hand, damping factor tand reveals the energy dissipated in the system with increase in the applied linear deformation. We thank the referee for this very interesting and thought-provoking point. Unfortunately, we do not believe that our short time DLS fits yield parameters with adequate accuracy to suggest quantitative correlations. This aspect should be addressed in future studies.

5. What is the significance of perfect data collapse in Fig 3.5f and partial data collapse in Fig. 3.9. In terms of strain/stress to which data collapse is observed? Would rheology data at multiple frequency help?

Reply - The excellent superpositions of the relaxation time data shown in Fig 3.5(f) suggest that the temporal evolution of the relaxation processes in all the

Laponite suspensions are self-similar when various additives are introduced in the sample, indicating that the underlying energy landscapes remain self-similar in the presence of these additives. Therefore, while the rate of the aging process is altered by incorporating additives, the underlying dynamical mechanisms such as the swelling of clay clusters and the exfoliation of single particles continue to happen, though at different rates that are determined by the nature of additives as explained earlier and in sections 3.3.1 and 3.3.2 of chapter 3.

The partial data collapse in Fig. 3.9 suggests that while all the samples exhibit self-similar nature in the linear viscoelastic (LVE) regime, both viscoelastic moduli G' for the different samples studied show different dependences on applied strain amplitude in the non-linear regime. This arises from disruption of the fragile sample microstructures at higher strains.

A protocol suggested by Winter and Chambon (Winter *et al.* Journal of Rheology, 30, 367 (1986)) can be helpful in investigating the sol-to-gel transition point in aqueous aging Laponite suspensions. In this protocol, rheological experiments (time test experiments for aging samples) can be performed at multiple angular frequencies. The intersection point of the plot of tan δvs . time performed at various frequencies is characterized as the sol-gel transition time for the aging samples. This is an exciting experiment to perform in future studies and we thank the referee for this suggestion.

6. Do figures 3.5f and 4.2b suggest a "additive-temperature" equivalence? There is only a mild acknowledgement of this on p 108 "effects are reminiscent of those arising from the incorporation of ionic additives at room temperature".

Reply – It is well known that an increase in temperature has a chaotropic effect on water structure because it breaks the hydrogen bonds in water. In aqueous Laponite suspensions, increasing suspension temperature also enhances the dissociation of Na⁺ ions from the Laponite platelets. The increased dissociation rate of Na⁺ ions enhances the interparticle electrostatic attraction, which dominates over structural changes in the water caused by raising the temperature of the suspension. Hence, while temperature has an equivalent effect as ionic additives such as NaCl or KCl where electrostatic interaction dominates over structural changes, the same cannot be claimed for the case when non-ionic additives are incorporated in Laponite suspensions.

7. Fig. 6.7 – How does G' at high temperature relate quantitively to degree of crosslinking? How different is this dependence compared to G' for a crosslinked rubber?

Does the frequency response confirm the "glassy" and "gel-like" response above and below LCST?

Reply – Increasing crosslinker concentration enhances the bulk modulus of the particles and hence the G'. The relevant data is plotted in Figs. 6.7a and 6.10a of the thesis. The increase in G' with increasing particle stiffnesses at a temperature above the LCST can be attributed to the higher crosslinking density present in the stiffer particles. Crosslinked rubber is highly elastic in comparison to microgels. Microgels such as PNIPAM contain water even in their completely collapsed state.

Our conclusions regarding the glassy/ gel-like/ liquid-like nature of the samples are based on a combined study of the frequency response and strain amplitude sweep oscillatory rheological measurements. Our frequency sweep data shown in Fig 6.8 exhibit the characteristics of soft glassy rheology at a temperature below the LCST and attractive gel-like nature at temperature above the LCST, as also reported in the literature. As shown in Figs. 6.8 a,d,g, below LCST, all PNIPAM suspensions investigated display approximately frequency independent G' and weakly frequency dependent G'' values, indicating the existence of slow glassy dynamics in these samples (ref. 36 of chapter 6). On the other hand, the frequency-dependent viscoelastic behaviour of suspensions of PNIPAM particles of intermediate and large stiffnesses near the LCST (figs. 6.8e and 6.8h respectively) reveals the presence of weak gels/ glasses. At temperature above the LCST, we observed increase in G' with frequency, together with a minimum in G'' (Fig. 6.8), which is characteristic of glasses or gels composed of hard attractive colloids [ref. 36–38 of chapter 6].

8. Fig. 7.16 – Do the particles deform due to shear? Is it reflected in "effective" contact area and the strength of interfacial polarization? Is it possible that there are force chains? In other words, is it possible that some particles deform more and carry larger amount of stress – leading to non-affine deformation?

Reply – PNIPAM particles are soft and can be easily deformed by applying shear. As the referee suggests, we do expect the moduli to be dependent on the effective contact area below the LCST and the strength of interfacial polarization above the LCST. Our dielectric data records the average response of the particles present in the sample. Force chains arise out of frictional contacts in granular media. We believe the main contribution to the rheology comes from the elastic stresses generated due to the deformation of PNIPAM particles under the applied strain amplitude.

9. How appropriate is the use of difference G'- G''?

Reply – We have used the difference between the storage and loss moduli (G'-G'') of the system as a quantitative measure of the relative rigidity of the sample. There can be other ways of characterising the relative rigidity, for example, $\tan \delta = G''/G'$ could also have been used.

10. Fig 9.6c / 9.9 - How reliable are these data? What is "residual noise"? How about torque sensitivity of the instrument at low strain.

Reply – The noise in the data we observe in Figs. 9.6c and 9.9 at very low strains arises due to the low torque sensitivity of the rheometer at very low strains. This has been referred to as residual noise in the literature (Journal of Rheology, **52**, 6, 1427-1458 (2008) and Journal of Rheology, **58**, 1, 43-62 (2014)). The data shown in Figs. 9.6c and 9.9 are for relatively liquid like samples and the observed noise in the G' and G'' at very low applied strain amplitudes (~ 0.2%) arises due to the low torque sensitivity of the instruments. At strain amplitudes greater than ~0.5%, we do not observe noise in G' and G''. We would like to point out here that we get noisy data for very few samples which are, as mentioned earlier, relatively liquid like. Hence, we can trust our data presented in Figs. 9.6c and 9.9.

Minor comments:

1. P226 - LCST becomes more continuous with increase in the crosslinker concentration...more continuous?

Reply – As we can see in Fig. 9.2a, there is an abrupt decrease in the size of the soft PNIPMAM particles near the LCST. Due to the higher osmotic pressure within soft core particles (characterised by low polymer crosslinking concentration), the polymer networks undergo rapid expansion upon incorporating water. On the other hand, sizes of stiff PNIPMAM particles decrease continuously with temperature near the LCST.

2. P232 – As discussed in more detail in chapter 6, demonstrate the characteristics?

Reply – In Fig. 9.6, we observed two-step changes in the viscoelastic moduli in some samples, which is a characteristic of attractive glasses/gels comprising hard colloidal particles. This behaviour has been discussed in more detail in section 6.3.2b of chapter 6.