Interface-Induced Anisotropy and the Nematic Glass/Gel State in Jammed Aqueous Laponite Suspensions

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ABSTRACT: Aqueous suspensions of Laponite, a system composed of disklike nanoparticles, are found to develop optical birefringence over several days, well after the suspensions solidified because of jamming. The optical anisotropy is particularly enhanced near the air—Laponite suspension interface over length scales of several millimeters, which is beyond 5 orders of magnitude larger than the particle length scale, suggestive of large-scale ordering influenced by the interface. The orientational order increases with time and is always greater for higher concentration of salt, higher concentration of Laponite, and higher temperatures of the suspension. Although weakly birefringent, Laponite suspensions covered by paraffin oil do not show any enhancement in optical anisotropy near the interface compared to that in the bulk. We suggest that the expedited structure formation near the air interface propagating progressively inside the sample is responsible for the observed behavior. We discuss the observed nematic ordering in the context of glass-like and gel-like microstructure associated with aqueous Laponite suspensions.
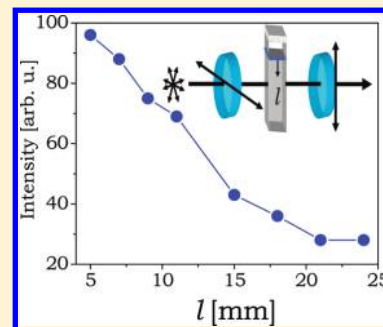
I. INTRODUCTION

Clays are ubiquitous in nature. Their nanoscopic size, anisotropic shape, apparently nontoxic nature, and low cost render them applicable in the paper, polymer, petroleum, paint, cosmetic, pharmaceutical, and food industries.[1] Clays have always attracted the attention of the colloidal community from an academic point of view as well.[2] Their layered nature, charge distribution, and microstructural richness have been the subjects of investigation over the last several decades.[3−5] Lately there has been a renewed interest in clays, and much work has been carried out to understand the microstructures and phase behaviors of aqueous clay suspensions.[6−8] Laponite, a synthetic hectorite clay, and its aqueous suspensions have been the subjects of intense investigation because of their perplexing phase behavior and industrial applications.[9] Aqueous suspensions of Laponite are known to show a spectacular increase in viscosity to form a soft solid-like transparent gel/paste that is not at thermodynamic equilibrium. The microstructure that causes very large increases in viscosity, however, is not clearly understood and has been a subject of debate over the last two decades.[10−19]

Laponite, hydrous sodium lithium magnesium silicate ($Na_{+0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]_{-0.7}$), is composed of disk-shaped nanoparticles with diameters of 25 to 30 nm and a thickness 1 nm.[9,20] The particle size distribution of Laponite is fairly monodisperse. Laponite is a smectite (i.e., layer-like) clay and belongs to a family of 2:1 phyllosilicates.[2] A single layer of Laponite consists of an octahedral magnesia layer sandwiched between two tetrahedral silica layers. The isomorphic substitution of magnesium

by lithium within the octahedral layer renders a permanent negative charge to the faces of a particle. The edge of a particle is composed of an oxide of silicon and oxides and hydroxides of magnesium (and lithium in very small amounts),[10] as suggested by the idealized crystal structure of Laponite.[9] The point of zero charge for MgOH corresponds to a pH of 12.5,[21] whereas that of magnesium oxide corresponds to a pH of 10−13.[22] Silicon oxide, however, is negatively charged beyond pH 3.5.[22,23] Nonetheless, the crystal structure of Laponite clearly indicates that the edge of Laponite must have a negative charge beyond pH 13. However, it is difficult to establish the point of zero charge associated with the edge precisely because the extremely small size of the particle hinders the estimation by a direct measurement. The conductivity measurements of Tawari and co-workers reported a positive edge charge for Laponite having a pH close to 10.[24] Laponite is hydrophilic, and its suspension in water above 1 vol % concentration has a soft solid-like consistency that supports its own weight.[25] The phase behavior of the aqueous suspension of Laponite has been studied and discussed in the literature over the past decade.[10−19] For a Laponite suspension having a 1 vol % concentration, mainly two kinds of microstructures have been proposed. The first one is an attractive gel structure formed by a network of particles connected via a positive edge and a negative face. The second proposed structure is that of a repulsive

glass wherein particles are self-suspended because of the repulsive environment without touching each other. Many groups have observed orientational order in aqueous suspensions of Laponite and other clay materials.[17,26−40] A small-angle X-ray scattering study on an aqueous Laponite B suspension for a concentration a little above 1 vol % demonstrated the existence of nematic-like orientational correlations with an order parameter of 0.55 that is comparable to that of liquid crystals,[32] suggesting the coexistence of weak order along with dynamic defects. Recently, a small-angle neutron scattering study on Laponite RD suspensions suggested two possibilities: "a long-range orientational order but short-range positional order of Laponite particles" or "short-range order for the repetition of the layers of Laponite discs without any order within each layer".[26] It is, however, important to note that these studies investigate essentially the bulk behavior.

In this work, we report on Laponite suspensions that develop optical birefringence over many days after going into a completely jammed state. We observe that an aqueous suspension of Laponite shows strong a enhancement in orientational order in the vicinity of the air/nitrogen interface that extends beyond spatial regions over orders of magnitude greater length scales than the particle length scale. Remarkably, an extent of order near the air interface continues to increase even though the material is in a physically jammed state.

II. MATERIAL AND METHODS

An aqueous dispersion of Laponite RD (Southern Clay Products) was prepared by dispersing it in deionized water of pH 10, unless otherwise mentioned, using a turrex drive. The sample was stirred vigorously for 45 min to ensure complete dissolution of the clay platelets. The detailed preparation procedure is discussed elsewhere.[10] In this work, we have primarily used a 2.8 wt % Laponite suspension with and without salt (NaCl). We have also carried out some experiments in the concentration range of 2−3.5 wt % as well as in the pH range of 9−13. The millimolar concentration of Na^+ due to externally added NaCl or NaOH is mentioned. Because the pH of water is adjusted using NaOH, a pH 10 system without any externally added salt has a Na^+ concentration of around 0.1 mM. This mentioned concentration of Na^+, however, does not include the concentration of Na^+ due to the dissociation of counterions associated with Laponite. The freshly prepared samples were placed in glass cuvettes with a square cross section (35 mm × 10 mm × 10 mm). Cuvettes of up to 30 mm in length were filled with the sample. In this study, we used two systems: one with a Laponite suspension−paraffin oil interface and another with a Laponite suspension−air interface. To ensure the absence of CO_2 contamination, we repeated some experiments with an N_2 atmosphere instead of air. We did not observe any noticeable difference when air was replaced with N_2. In this article, we will therefore use the term air interface to represent both air and the N_2 interface. In the oil interface case, the remaining space in the cuvette was filled with paraffin oil. In both the cases, the Teflon lid of the cuvette was tightly sealed with an epoxy adhesive to prevent any mass transport (paraffin oil, air, or water vapor) across the cuvette. This rules out the evaporation of water in cuvettes having air interfaces. (It should be noted that the volume of air was less than 15% of the volume of the Laponite suspension.) The samples eventually solidify so as to sustain their own weight when inverted. Precaution was taken to prevent any movement of the air or paraffin oil bubble because the deformation induced by the same may influence the orientation of Laponite particles in the suspension. Some of the Laponite suspension samples were filtered using a Millipore Millex-HV 0.45 μm filter before the cuvettes were filled.

In a uniaxially anisotropic homogeneous medium, the refractive indices of polarized light with the electric field parallel and perpendicular to the anisotropy axis become different. This results in optical birefringence. Linearly polarized light upon traversing the sample becomes elliptically polarized in general. It can be shown that the intensity of light transmitted across a uniaxial sample placed between two orthogonal polarizers is given by $I_T = I_0 \sin^2(2\alpha) \sin^2(\Delta n k_0 \delta/2)$,[41] where I_0 is the intensity of the incident light, Δn is the difference in refractive index along the axis and perpendicular to the axis, k_0 is a wave vector in free space $(2\pi/\lambda)$, δ is the thickness of the sample, and α is an angle between the ordinary axis of the anisotropic medium and the polarizer axis. Therefore, the transmitted intensity is a measure of the birefringence (Δn).

We conducted the birefringence experiments on aqueous Laponite suspensions wherein the transmittance of light was measured through the sample kept in between crossed polarizers. In these experiments, because of the large (macroscopic) beam size and sample thickness, the measured optical birefringence is an average over variously oriented domains. The microscope image and the minimal scattering from the sample indicate small domain structures over length scales of a few micrometers.

A polarizing microscope (Olympus BX-51) was used to investigate the optical transmission properties of the samples at 5× magnification. The axes of the polarizer and analyzer were parallel and perpendicular, respectively, to the axis of the cuvette. The spectrum of the transmitted light was recorded with an Ocean Optics USB 400 spectrometer connected to the trinocular port of the microscope via an optical fiber. The intensity of the transmitted light was measured as a function of time elapsed since the preparation of the sample along the length of a cuvette. Prior to each spectral measurement on the Laponite suspension samples, the intensity of the light through crossed polarizers was measured to account for the fluctuations in the intensity. No resonant spectral features were noticed in the transmittance of light in the wavelength range of 450−700 nm. We also used a He−Ne laser (632 nm and 1 mW) and sheet polarizers to carry out birefringence experiments with a smaller beam size of about 0.6 mm to validate our optical microscope measurements. The intensity beyond the analyzer was measured using a photodiode coupled to an amplifier. A minimal amount of scattering was observed from the path of the laser beam within the sample. The polarizer and analyzer were simultaneously rotated, and the intensity of the transmitted light was also measured as a function of the rotation angle.

III. RESULTS

Figure 1 shows a typical spectrum of the transmitted light through crossed polarizers with and without sample (a Laponite suspension). It can be seen that the intensity of transmitted light is significantly enhanced by the presence of the sample. We have used two types of samples: suspensions filtered with a Millipore Millex-HV 0.45 μm filter and suspensions without any filtration. As shown in Figure 1, filtration does not have any noticeable influence on the intensity of the transmitted light. To compare the intensity of transmitted light relative to that of crossed polarizers without any sample, we define the normalized transmittance as $T_N = [\int(I_S/I_{NS}) \, d\lambda]/[\int \, d\lambda]$. Here, I_S and I_{NS} represent the intensity of transmitted light through crossed polarizers with and without a sample, respectively. In our case, normalized transmittance $T_N = 1$, which therefore represents no birefringence ($I_S = I_{NS}$), suggesting the isotropic nature of the sample. However, $T_N > 1$ represents birefringence ($I_S > I_{NS}$) indicating anisotropy or an orientational order of the clay platelets.

We measured the transmittance of the sample through crossed polarizers with air and oil interfaces as a function of the distance from the free interface. The measurements could be taken only
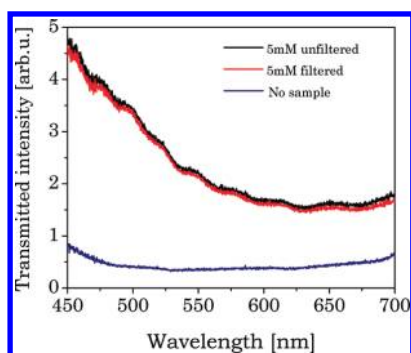
Figure 1. Spectrum of the transmitted light through the crossed polarizers with an unfiltered sample (black line) and a filtered sample (red line) of 2.8 wt % Laponite with 5 mM NaCl. The intensity through the crossed polarizers with no sample is also shown in the plot (blue line, bottom curve). The experiments were carried out at a location about 25 mm away from the air interface.
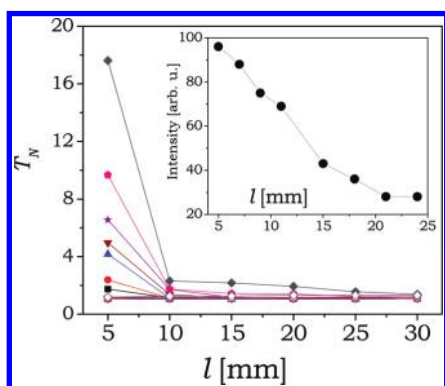

Figure 2. Normalized transmittance plotted as a function of distance from the interface along the length of the cuvette for a 2.8 wt % Laponite suspension without externally added salt at different times since preparation (day 2, squares; day 4, circles; day 6, up triangles; day 8, down triangles; day 10, stars; day 14, pentagons; and day 18, diamonds). The filled symbols are for the sample with the air interface, and the open symbols denote the samples with a paraffin oil interface. The inset shows the intensity measured through cross polarizers for a sample having an air interface using a He–Ne laser for a 5 mM NaCl suspension 9 days after preparation.

every 5 mm because the optical beam width was large in the microscope even with the optical aperture kept to a minimum. We have plotted the normalized transmittance measured at various locations away from the interface for suspension samples having air–Laponite and oil–Laponite interfaces at various times in Figure 2. It can be seen that the normalized transmittance is enormously increased if the light beam's path is closer to the interface for samples having air interfaces. The normalized transmittance rapidly decreases for paths more distant from the interface on length scales of a few millimeters and becomes almost constant in the bulk. Interestingly, the normalized transmittance increases with the age of the sample much more strongly near the interface than in the bulk. However, unlike samples with an air interface, the transmittance of beams with paths closer to the oil–Laponite suspension interface is observed to be same as the bulk value, which is also equal to transmittance in the bulk sample with an air interface. We also carried out similar experiments using a He–Ne laser. In these experiments, the laser beam
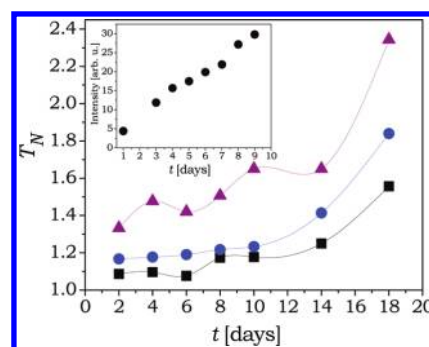

Figure 3. Normalized transmittance 25 mm away from the interface plotted as a function of time elapsed since the preparation of a 2.8 wt % Laponite suspension for various salt concentrations (squares, 0.1 mM; circles, 3 mM; and triangles, 5 mM NaCl). The lines are only guides to the eye (spline fits). The inset shows the He–Ne laser intensity measured through crossed polarizers for a suspension containing 5 mM salt at the same location.

width was about 0.6 mm. The inset in Figure 2 shows the intensity of transmitted light through a 2.8 wt % 5 mM NaCl sample having an air interface 9 days after preparation. It can be seen that the transmittance decays rapidly away from the interface and plateaus out in the bulk (about 20 mm from the interface).

Furthermore, in Figure 3 we have plotted the normalized transmittance through the bulk of the samples (25 mm away from the interface) as a function of the time elapsed since sample preparation. It can be seen that the transmittance under the crossed polarizers increases with the age of the samples. In addition, for the samples containing a higher concentration of salt, the normalized transmittance is always observed to be higher. The inset in Figure 3 shows the intensity of transmitted light from a He–Ne laser at a 632 nm wavelength through a sample with 2.8 wt % 5 mM NaCl (and measured 25 mm away from the air interface). It is clear that the transmittance increases with time elapsed after the sample preparation. We did not observe any noticeable differences in the transmittance for samples having an air interface and an oil interface when the optical path was about 25 mm away from the interfaces.

To understand the effect of the salt concentration and age of the sample on the enhancement of optical transmittance, we have plotted in Figure 4 the integrated optical transmittance on days 2 and 21 along the length of the cuvette for 0.1, 3, and 5 mM salt concentrations for Laponite suspensions having an air interface. On day 2, although birefringence is observed in the sample, which increases with the concentration of salt, no noticeable increase is observed near the interface. On day 21, however, the interface can be seen to be playing a dominant role even beyond 10 mm toward the bulk but keeping within the trend of greater birefringence for higher concentrations of salt.

In addition to the salt concentration, we also studied the effect of the pH of the suspension, the concentration of Laponite, and the temperature at which the sample undergoes aging. For the 6-day-old 2.8 wt % Laponite suspension with 5 mM NaCl having different pH values, the intensity of light through the crossed polarizers 5 and 25 mm away from the interface is described in Figure 5. We observe huge increases in intensity near the interface with increases in the pH of the suspension from 9 to 11. The enhancement near the interface is observed to be significantly stronger than that in the bulk. Interestingly, at pH
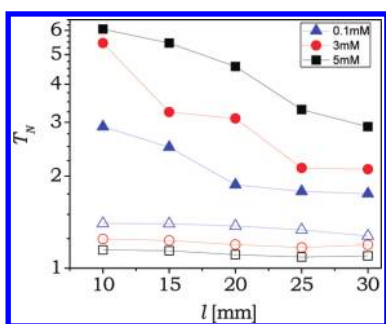
Figure 4. Normalized transmittance along the length of a cuvette away from the interface for 2.8 wt % Laponite suspensions having different concentrations of salt (squares, 0.1 mM; circles, 3 mM; and triangles, 5 mM NaCl; the line is a guide to the eye) 2 days (open symbols) and 21 days (filled symbols) after the preparation of the sample.
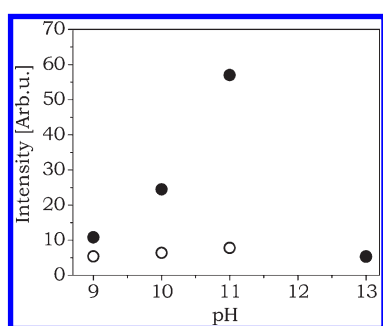

Figure 5. Effect of pH on the birefringence behavior of a 6-day-old 2.8 wt % Laponite suspension having 5 mM NaCl. Open symbols represent the behavior in the bulk (25 mm away from the interface), and filled symbols represent the behavior near the interface (5 mm away from the interface).

13 no significant enhancement in birefringence either in the bulk or near the interface is observed.

The birefringence behavior for a 6-day-old Laponite suspension having various concentrations (2, 2.4, 2.8, and 3.5 wt %) and 5 mM NaCl close to and far away from the interface is described in Figure 6. It can be seen that for 2 wt % samples there is no evident difference in birefringence in the bulk or near the interface. However, for higher-concentration samples, an enhancement in birefringence near the interface is far more pronounced than that in the bulk. We also studied the birefringence behavior of a 2.8 wt % 5 mM NaCl sample at pH 10 aged at 60 °C. Figure 6 shows that increases in temperature enhance the intensity of transmitted light more near the interface than in the bulk.

To investigate the orientation of the anisotropy axes for the different interfaces, we measured the transmitted intensity as a function of the angle between the cuvette long axis and the input polarizer. This was accomplished by rotating both the polarizer and analyzer by the same angle simultaneously while keeping the cuvette fixed. This ensured that the nonhomogeneity of the sample did not affect the measurements as the beam passed through exactly the same region of the sample. Figure 7 shows that the transmitted intensity is almost sinusoidal. This observation confirms that we have a uniaxial system where the transmitted intensity is given by $I_T = I_0 \sin^2(2\alpha) \sin^2(\Delta n k_0 \delta/2)$, where α is the angle between the ordering axis in the sample and the polarization axis. The lines in the plot show fits of the expression $I_T = I_{noise} + \tilde{I}_0 \sin^2(2\theta + \delta)$ to the experimental data.
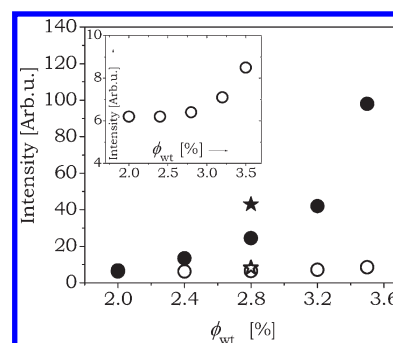

Figure 6. Effect of the concentration of Laponite on the birefringence behavior of a 6-day-old suspension at pH 10 with 5 mM NaCl. Open symbols represent the behavior in the bulk (25 mm away from the interface), and filled symbols represent the behavior near the interface (5 mm away from the interface). Circles represent experiments carried out on sample aged at 25 °C, and stars represent those at 60 °C. The inset shows the bulk behavior as a function of concentration at 25 °C.
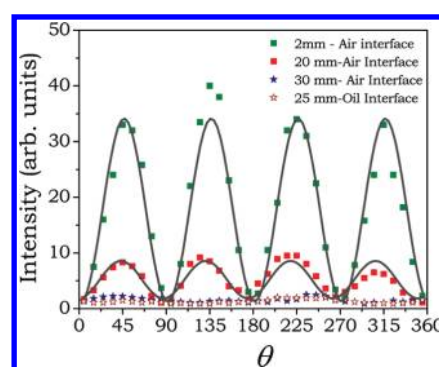

Figure 7. Intensity variation for a 2.8 wt %, 5 mM salt system 12 days after preparation plotted as a function of θ, the angle between the cuvette long axis and the input polarizer, obtained by simultaneously rotating the polarizer and analyzer with respect to the sample. The variations obtained along the length of the cuvette for samples with air and oil interfaces are shown.

For both fits, δ is observed to be smaller than 1°. The maximum intensity is observed when the electric field is at an inclination of almost 45° to the long side of the cuvette, indicating that within the accuracy of the measurements the anisotropy axes match the cuvette long axis and the interface. The modulation of the transmittance with the angle was also measured at various distances from the air interface. The figure shows that at about 2 mm from the interface the magnitude of transmittance that varies sinusoidally is significant. The intensity decreases with increasing distance from the interface. Beyond a distance of 30 mm from the air interface, the modulation becomes minimal so that the sinusoidal variation cannot be clearly observed because of noise and the inhomogeneous anisotropy of the sample. The transmittance in the oil interface samples is not significant as compared to that in the bulk and very closely matches the transmittance measured at a distance of 30 mm from the air interface. The transmittance variation indicates a global anisotropy that stems from a long-range directional ordering within the Laponite suspension. This presumably arises from the orientational ordering of the meso structures in the jammed Laponite suspension. Interestingly, the angle does not depend on the salt concentration, indicating that only the interface may play a role. The

Table 1. Conductivity and Debye Screening Length of an 18-Day-Old 2.8 wt % Laponite Suspension

concentration of salt (mM)	conductivity (μS/cm)	Debye screening length (nm)
0.1	956	3.1
3	1250	2.8
5	1380	2.71

angular dependence is present in the sample only after a period of 8 days.

IV. DISCUSSION

We have investigated the optical birefringence in jammed aqueous Laponite suspensions with air and oil interfaces. The various observations reported in this study can be broadly divided into four topics: (1) The observation of anisotropic orientation and how it is influenced by the aging time, concentration of salt, concentration of Laponite, pH of the suspension, and temperature. (2) An increase in birefringence while the system is in a physically arrested state. (3) The effect of an interface, air, and/or paraffin oil on the microstructure. (4) The observation of interface-induced anisotropy over length scales that are several orders of magnitude greater than the particle length scale.

In aqueous suspensions of Laponite, the disk-like shape and the interplay between attraction and repulsion among the particles influence the morphology and phase behavior. Many groups have proposed that ergodicity breaking in aqueous suspensions of Laponite beyond 1 vol % is due to repulsive interactions among Laponite particles, leading to the formation of a Wigner glass.[8,12,14,42] Orientational order in such a situation, where Laponite particles are surrounded by neighboring particles because of repulsive interactions (without physically touching each other), can be analyzed by Onsager's theory for a suspension of hard disks. The reduction in excluded volume by aligning the particles drives the isotropic–nematic transition in anisotropic systems.[43] A suspension of hard discs, for an aspect ratio of $a\ (= L/D)$, is expected to demonstrate isotropic to biphasic and biphasic to nematic transitions above volume fractions $\phi_{i-b} = 0.33a$ and $\phi_{b-n} = 0.45a$, respectively. In the biphasic state, both nematic and isotropic phases coexist. For Laponite RD, whose aspect ratio is in the range of 25–30, a concentration at which the isotropic to biphasic transition should be observed is 2.75 wt % whereas a nematic state is possible only above 3.8 wt %.[10] However, to have a self-suspended state of Laponite particles originating from repulsive interactions, for the concentration of 2.8 wt %, Laponite particles need to maintain an average distance of 40 nm from each other.[10,13] A recent small-angle X-ray scattering study by Ruzicka and co-workers[12] carried out for similar concentrations of Laponite without any externally added salt aged for around 50 h reports a peak in the structure factor at $Q = 0.17$ nm^{-1} corresponding to an interparticle distance of 37 nm. Because Laponite has a diameter of 25–30 nm, the jammed state is proposed to be a repulsive glass. Ruzicka and co-workers[12] also carried out theoretical and simulation studies with a Debye screening length in the range of 5–10 nm that showed agreement with their experimental study by considering a Wigner (repulsive) glass picture.

Interestingly, we observe that birefringence associated with samples having higher concentrations of salt was always greater at

any aging time. To judge this behavior from the point of view of a repulsive glass scenario, information on the Debye screening length associated with the same is necessary, which requires a certain concentration of cations (Na$^+$ ions) and anions (Cl$^-$ ions) in the suspension. The concentration of ions can be obtained from the conductivity of Laponite suspensions having varying concentrations of salt and is given by $\sigma = e(\mu_+n_+ + \mu_-n_-)$,[44] where σ is the conductivity, μ_+ and μ_- are the mobilities of cations and anions, respectively, n_+ and n_- are the concentrations of cations and anions, respectively, and e is the electron charge. The presence of Cl$^-$ in the suspension is due to only externally added salt whereas Na$^+$ is present because of externally added salt as well as counterions. When we ignore the concentration of OH$^-$,[13] n_- can be directly obtained from the concentration of externally added salt. Therefore, with a knowledge of the mobilities of Na$^+$ and Cl$^-$ ($\mu_{Na} = 5.19 \times 10^{-8}$ m^2/s V and $\mu_{Cl} = 7.91 \times 10^{-8}$ m^2/s V)[45] and the conductivity of a Laponite suspension, n_+ can be easily estimated, which in turn can be used to estimate the Debye screening length. In Table 1, we report the ionic conductivity (σ) of a 2.8 wt % aqueous Laponite suspension 18 days after the preparation of a suspension along with Debye screening lengths for 0.1, 3, and 5 mM salt concentrations. It can be seen that increases in the concentration of salt cause decreases in the Debye screening length. This observation suggests decreases in repulsive interactions with increases in the concentration of salt. Figures 3 and 4 show that the enhancement in birefringence is faster with increases in salt concentration. As discussed in the Introduction, enhancement of viscosity is also faster with increase in salt concentration.[10,25] If we believe that enhancements in viscosity and birefringence in 2.8 wt % Laponite suspensions with varying salt concentration are due to the same microstructure, then a repulsive interaction scenario cannot explain the faster buildup of Wigner glass at higher salt concentrations. Interestingly, enhancements in viscosity and birefringence seem to have a significant correlation. As reported in the literature, increases in the concentration of Laponite and temperature causes faster increases in the viscosity of its aqueous suspension.[25,46] Similarly, we also observe a greater enhancement in birefringence with increases in concentration and temperature as shown in Figure 6.

The other popular proposal for a microstructure of an aqueous Laponite suspension is an edge-to-surface attractive interaction originating from a positively charged edge and a negatively charged face, leading to a gel. The most popular attractive configuration is a house of cards structure where there is an edge-to-surface attractive interaction among the Laponite particles as shown in Figure 8a, which produces a gel-like structure.[15,47−50] Recently Jonsson et al.[19] proposed another possibility wherein edge-to-surface association occurs in an overlapped coin configuration (Figure 8b). Their Monte Carlo calculations predict that for ionic concentrations in the range of 10 to 60 mM, the overlapped coin configuration has a deeper minimum compared to the perpendicular edge-to-face configuration. To have two particles approach each other to have an edge-to-surface interaction, they need to overcome a repulsive barrier between them. With an increasing concentration of salt, repulsion among particles decreases, thus decreasing an energy barrier for particles to approach each other. Interestingly, increases in viscosity are known to be expedited in the presence of salt.[10,25] Because the phenomenon viscosity enhancement can arise from the formation of edge-to-surface bonds, this observation suggests the possibility of a corelation between orientational anisotropy and
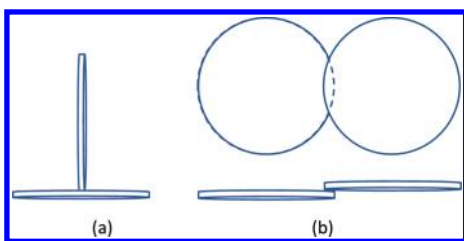
Figure 8. Schematic of possible edge-to-surface attractive interactions. (a) Edge-to-surface perpendicular interaction (T-shaped) leading to a house-of-cards structure. (b) Edge-to-surface overlapping coin configuration proposed by Jonsson et al.[19]

attractive associations in Laponite suspensions. As shown in Figure 5, the Laponite suspension shows a greater birefringence with increases in pH of up to 11; however, it does not show any noticeable birefringence at pH 13. As suggested in the Introduction, at pH 13 the edge of a Laponite particle possesses a negative charge; therefore, edge-to-face interactions are certainly not possible at that pH. However, with increases in pH from 9 to 11, a greater ionic strength of the suspension (due to a greater concentration of NaOH in a high-pH system) may lead to greater birefringence.

Overall, the repulsive glass scenario does not explain the salt concentration dependence of order formation, and the attractive gel scenario does not explain the interparticle distance observed experimentally. We therefore feel that the issue of the microstructure of the aqueous Laponite suspension is still open and further spectroscopic studies such as SAXS need to be conducted at different concentrations of salt and different pH values over a greater span of aging times.

It is usually observed that the viscosity of a 2.8 wt % Laponite suspension increases very rapidly after mixing Laponite with water such that it supports its own weight within a few hours of sample preparation. However, as shown in Figures 2 and 3, it takes a few days for the suspension to show significant birefringence. This behavior suggests that the motion of the particles in a jammed state is not completely frozen and undergoes local orientational adjustments that keep evolving as a function of time. Eventually, the clay platelets form microdomains with the director of each domain oriented in a particular direction. It is difficult to comment on how this process occurs unless the precise cause of such a massive increase in viscosity is known. If we assume that the repulsive interactions cause the increase in viscosity, then in a jammed state order formation can take place by the movement of individual Laponite particles. If edge-to-surface interactions are favored, two possibilities exist as described in Figure 8a,b. According to Jonsson and co-workers,[19] an overlapped coin configuration has a deeper but much narrower free-energy minimum whereas the T configuration has a shallower but broad minimum. Therefore, there is a possibility that in a jammed state, edge-to-surface interactions may undergo a transition from the T configuration to the overlapped coin configuration during an aging process that not only increases its viscosity further but also induces orientational ordering. Owing to the restricted mobility of Laponite particles in a jammed state, such restructuring is expected to be very slow in the bulk of the material, as observed in Figures 2 and 3.

Now we turn to the effect of the interface on the morphology of Laponite suspensions. We observe an alignment of Laponite particles near an air interface, which otherwise is absent in a

sample having an interface with paraffin oil. Figure 7 suggests that Laponite particles are oriented almost perpendicular to the interface (where the surface normal of a disk is parallel to the interface). It is apparent from Figure 2 that birefringence increases with the sample age much more rapidly at the interface than in the bulk. Thermodynamically, the migration of Laponite particles to the air interface will be favorable if it causes a decrease in the surface energy of the air–water interface. The surface energy (interfacial tension) of the water–air interface is 73 mJ/m^2,[51] and that of the paraffin oil interface is lower at 48 mJ/m^2.[52] Although there is no report in the literature about the effect of Laponite on the surface energy of the air–water or air–oil interface, Na-montmorillonite, which has a similar crystal structure to that of Laponite, is reported to increase the surface energy of the water–air interface.[53] Owing to the similarity in the structure,[2] if we assume that Laponite also increases the surface energy of the water–air interface, then the migration of Laponite particles toward the interface will not be favored. Furthermore, such a scenario will repel Laponite from the water–air interface, creating a thin layer near the air interface that is depleted of Laponite particles.[54] The surface energy drive, therefore, should be ruled out as a reason behind such ordering.

The other possibility discussed in the literature that may lead to an understanding of the observed phenomenon is the greater mobility of the particles near the interface. It has been proposed that in glassy materials, particles near a free surface experience a structural cage only from the inner side, which endows them with better mobility than the bulk and may expedite aging.[55] It is important that in the bulk of the Laponite suspension, Laponite particles are surrounded by neighboring particles that significantly hinder their mobility, driving the system into an arrested state.[56] However, because the particles near the air interface are depleted from a very thin layer near the interface, their mobility is expected to be enhanced from one side. Figure 3 suggests that aging in a 2.8 wt % Laponite suspension involves constructing an order as a function of time. Therefore, it is possible that the inherent tendency of Laponite particles to form an ordered state (specific microstructure that leads to ordering is still an open question) is amplified by the greater mobility of the particles near the free surface. This phenomenon may drive the nematic ordering of the particles at the air interface, which otherwise is difficult in the bulk because of hindrance from all sides. Recently, Mamane and co-workers[57] studied thermal fluctuations of the free surface of an aging Laponite suspension and observed that older Laponite suspension samples exhibit bursts of fluctuations that demonstrate non-Gaussian dynamics compared to younger Laponite suspensions. The concentration of Laponite used by Mamane and co-workers (2.5 wt %) is not very different from that used in the present study (2.8 wt %). They also suggested that the observed behavior could result in an enhanced mobility of Laponite particles near the free surface. The perplexing behavior, however, is that the greater ordering near the interface than in the bulk is absent in the case of the paraffin oil interface because the physical hindrance toward the interface will not be present in this situation. There may be a possibility that oil-specific interactions (or the absence of interactions) of Laponite, because of its organophobic nature, may be responsible for the prevention of ordering. Nonetheless, it appears from the observed behavior that the faster structure (gel or glass) formation near the air interface that progressively percolates toward the bulk is responsible for the observed behavior. Changes in the interaction potential around the particles near the air interface

may also drive such phenomena. The absence of structure formation in the oil interface system, the reason for which is not entirely clear to us at this moment, does not lead to birefringence near the interface. To have a better understanding of this behavior, SAXS studies need to be carried out in the vicinity of the air or oil interface.

An astonishing result of the present work is that the influence of order in samples having an air interface is observed beyond 5 orders of magnitude greater length scales than for the particle diameter (the particle diameter is 30 nm, but order is observed beyond 5 mm) as well as the average interparticle distance. Furthermore, the depth over which the interface seems to be an influence is observed to increase in the presence of salt. Stevenson and Wolynes[55] suggested that enhanced mobility at the surface percolates into the bulk through collaborative dynamics. The depth up to which the effect is observed would then be determined by the length scale of the cooperativity. Considering a recent report in which disorder on the surface destroys long-range order in the bulk (percolation of the surface phenomenon to the bulk),[58] the present observation, which demonstrates percolation to the bulk, may not be surprising. Again, if edge-to-face interactions are existent, the formation of an energetically preferred overlapped coin configuration near the interface may trigger the formation of the same microstructure into the bulk of the material like a zipping phenomenon.[59]

Finally, we concur that our results raise more questions about the phase behavior of aqueous Laponite suspension than provide answers. We believe that spectroscopic investigations near the interface and realistic simulations on charged disks may lead to further insight into the observed phenomena.

V. CONCLUSIONS

We study the birefringence behavior of aqueous suspensions of Laponite for samples having air and paraffin oil interfaces. We observe that for both types of interfaces, the suspension is weakly birefringent in the bulk. In the case of the air interface, however, the suspension shows much larger birefringence near the interface, suggesting a nematic order whose effect percolates beyond a 5 order of magnitude greater length scale than the particle length scale below the surface. No such behavior is observed for the Laponite suspension with an oil interface. In addition, the order increases with time even though the suspension is in a physically jammed state. Interestingly, at any aging time as well as location from the interface, greater order is observed for greater concentrations of salt and Laponite in the suspension.

We believe that, owing to its anisotropic shape, Laponite particles in an aqueous suspension with a 2.8 wt % concentration have an inherent tendency to be set in order. However, because the structural arrest precedes ordering, the system demonstrates weak order in the bulk. It appears that anisotropic structure formation, which leads to ergodicity breaking in the suspension, originates near an air interface. We believe that the cooperative dynamics of particles near the interface are responsible for a prorogation of the surface phenomenon into the bulk over length scales that are several orders of magnitude greater than the particle dimensions. Further spectroscopic investigations to establish the structure and the ordering mechanism are required.

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