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Orientalional order in a glass of charged platelets with a concentration gradient

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Colloidal dispersions of anisometric particles can display dynamical arrest and ordering involving both translational and rotational degrees of freedom. We show that orientational order can develop in glassy colloidal dispersions of charged platelets when a concentration gradient is imposed through solvent evaporation. Our model system of Laponite (LRD) platelets in deionized water has been extensively studied for its ergodic to non-ergodic transitions, and the existence of an underlying isotropic–nematic phase transition has been a subject of debate. We use small-angle X-ray scattering, dynamical light scattering and birefringence to show that the orientational order we observe does not result from an underlying, uniquely determined equilibrium state with orientational order, but from plastic deformation of the colloidal glass.

1 Introduction

Soft solids formed from colloidal dispersions are intriguing states of matter whose solid-like nature is attributed either to the formation of percolating networks (in gels) or to emerging topological constraints and dynamical correlations from crowding (in glasses). In this context, soft solids formed from anisometric particles such as clays are interesting because they can display arrest and ordering not only of translational but also rotational degrees of freedom. Experiments, simulations, and theory in fact suggest very rich state diagrams for both hard and soft particles with anisotropic interactions, featuring equilibrium phases like isotropic liquids1–3 and nematic liquid crystals (with long-range orientational but no positional order),1–3 as well as arrested states with slow translational and/or orientational degrees of freedom, such as orientational glasses (with slow rotations),1–3 ‘simple’ glasses (with slow translations),2 or double glasses (with slow rotations as well as translations).3,8–10

Several studies over the past years have demonstrated that dispersions of plate-shaped clays1–3 and related systems8–14 can undergo disorder-to-order transitions, and that these transitions can be true, equilibrium liquid crystal phase transitions when they occur in the ergodic sol region of the state diagrams. For Laponite (LRD) dispersions, observations of such clear-cut equilibrium transitions are generally pre-empted by dynamical arrest. The fact that orientational order may still develop despite slow dynamics and significant viscoelasticity is nevertheless an experimentally well-established fact,10,14–17 although in the case of Laponite (LRD), the relationship between dynamical arrest and observations of orientational order is not clear.

Here we use \( C_w = 3.0 \text{ wt}\% \) dispersions of Laponite (LRD) in deionized water to show that orientational order can develop in glassy dispersions of charged platelets when a concentration gradient is imposed through solvent evaporation. In deionized water, Laponite exists as less than 1 nm thick discs with diameters of approximately 25 nm. The particles carry a net negative surface charge and negligible rim charges. At a concentration of \( C_w = 3.0 \text{ wt}\% \) in deionized water, Laponite is reported to form orientationally disordered, repulsive ‘Wigner’ glasses whose translational as well as rotational dynamics slow down with time.10,18–24 A recent study23 indicates that interparticle attraction may gain influence at aging times beyond the timescale associated with the initial glass formation, although without altering the observed structure of the glass.

2 Experimental

We prepared our samples at \( C_w = 3.0 \text{ wt}\% \) Laponite (LRD) in deionized water following the procedure proposed by Bonn et al.9 All samples were stirred for 30 min after mixing before being suction filtered through a 0.8 \( \mu \)m pore filter. The time of filtration is \( t_w = 0 \). For \( t_w > 0 \) the concentration of particles was either increased by slow evaporation of the solvent water, or kept constant for a set of sealed reference samples. The evaporation process was conducted either under ambient conditions or in a protected \( N_2 \) atmosphere; the procedures were found to...
yield the same birefringence patterns. At waiting times in the range 2 weeks < \( t_w < 3 \) weeks, the dispersions were investigated by dynamical light scattering (non-evaporated samples), and by small-angle X-ray scattering and birefringence imaging (evaporated and non-evaporated samples). The waiting times are well beyond the timescales associated with repulsive glass formation,\(^{22,23}\) and also beyond the timescale for which attractive interactions have been suggested.\(^{24}\)

### 3 Results and discussion

#### Dynamical light scattering

We use dynamical light scattering (DLS, Fig. 1a) to confirm that, in agreement with previous studies,\(^{18,22,23}\) our \( C_w = 3.0 \) wt% samples can be interpreted as glasses. Because samples are non-ergodic on the experimental timescale, the intermediate scattering function \( f_s(\vec{q}, \tau) \) is obtained from the measured time autocorrelation function \( g_s(\vec{q}, \tau) \) as\(^{25-27}\)

\[
f_s(\vec{q}, \tau) = 1 + Y(g_s(\vec{q}, \tau) - g_s(\vec{q}, 0) + 1)/2 - 1). \tag{1}
\]

Here \( Y = \langle I(\vec{q}, \tau) \rangle / \langle I(\vec{q}, 0) \rangle \) with \( \langle I(\vec{q}, \tau) \rangle \), being the time-averaged brightness of the speckle yielding \( g_s(\vec{q}, \tau) \), and \( \langle I(\vec{q}, 0) \rangle \) the average brightness of a large number of sampling points. The fit of \( f_s(\vec{q}, \tau) \) to a function

\[
f_s(\vec{q}, \tau) = A \exp(-\tau/\tau_1) + (A - 1)\exp(-\tau/\tau_2)^\beta \tag{2}
\]

(Fig. 1a), yields \( \tau_1 = 0.01 \) ms and \( \tau_2 = (\tau_2/\beta) \Gamma(1/\beta) = 7 \times 10^8 \) s (with \( \beta = 0.3 \)). Because of the limited range in \( \tau \), the latter value is a lower bound on \( \tau_2 \). The non-ergodicity parameter, obtained from \( f_s(\vec{q}, \tau) \) in the limit \( \tau \to \infty \) (where \( g_s(\vec{q}, \tau) \to 1 \)), assumes values \( f_s(\vec{q}, \infty) > 0.9 \) at \( t_w = 3 \) weeks. This shows that the majority of the scattered intensity comes from density fluctuations that are frozen-in on the experimental timescale.

We also attempt to assess the rotational dynamics with depolarized DLS (Fig. 1a), and measure the time autocorrelation function \( g_0(\vec{q}, \tau) \) that contains contributions both from translational and rotational correlations. The nearly flat behaviour of the resulting intermediate scattering function \( f_0(\vec{q}, \tau) \) suggests, in accordance with previous studies,\(^{18}\) that rotational dynamics are also arrested.

#### Small-angle X-ray scattering from non-evaporated samples

Small-angle X-ray scattering (SAXS) experiments on such non-evaporated samples give isotropic scattering patterns indicating no net orientational order and only short-range positional order (Fig. 1b), expected from crowding (with a \( C_w = 2.0 \) wt% sample having less structure factor scattering than a \( C_w = 3.0 \) wt% one). To rationalize this, we calculate the theoretical volume \( V_s \) available to each Laponite platelet at complete delamination, assuming that \( N \) particles of a \( C_w = 3.0 \) wt% dispersion occupy and freely rotate within \( N \) non-overlapping spheres of radius \( r_s \). The empirical formula for Laponite is \( \text{Na}_0.7\text{Mg}_{5.5}\text{Li}_{0.3}\text{Si}_8\text{O}_{24}\text{H}_4 \) per unit cell.\(^{24}\) With each 25 nm Laponite platelet containing about 50 \( \times 50 = 2.5 \times 10^3 \) unit cells,\(^{28}\) we find that a single Laponite platelet has a molecular weight of \( 1.9 \times 10^6 \) g mol\(^{-1}\), so that a \( C_w = 3.0 \) wt% dispersion has a platelet concentration of \( N/V = 9.5 \times 10^{11} \) m\(^{-3}\), which is then also the concentration of spheres.

Now, if these spheres are randomly close packed (at a packing fraction 64%), we find that a total dispersion volume \( V \) has a volume of 0.64V that is divided into \( N \) spheres, so that the volume per sphere is \( V_s = 0.64V/N = 6.8 \times 10^{-23} \) m\(^3\). The spheres therefore have a radius of \( r_s = (3V_s/4\pi)^{1/3} = 25 \) nm. Such a Laponite glass would be non-connected and structurally homogeneous on length scales above roughly 50 nm, corresponding to a structure factor \( S(q) < 1 \) for \( q \lesssim 0.13 \) nm\(^{-1}\). This is in good agreement with the experimental data, which deviate from the calculated form factor for \( q \lesssim 0.15 \) nm\(^{-1}\) (Fig. 1b). The DLS and SAXS data are therefore consistent with the interpretation of non-evaporated \( C_w = 3.0 \) wt% samples as non-connected, double glasses, with neither long-range orientational nor translational order (see Fig. 2a). For reference, we note that the above calculations based on a close packing of spheres of radius \( r_s = (25/2) \) nm (with a packing fraction of 74%) imply that some local ordering is geometrically required for Laponite suspensions at platelet concentrations \( C_w > 29 \) wt%.
appearing at the interface near the end of this time series, implies a
Crossed linear polarizers were oriented at 45° with the vertical capillary axis.
sample, showing the central part of a capillary imaged at successive waiting times.
interface. 10 mm from the interface, at the end of the time series, and (e) just below the
temporal plot of developing birefringence in an evaporating
Fig. 2a) Schematic of the structure of an isotropic Laponite glass and (b) of a
Laponite glass with evaporation-induced orientational order. (c) A spatio-
temporal plot of developing birefringence in an evaporating Cw = 3.0 wt% LRD
sample, showing the central part of a capillary imaged at successive waiting times.
Crossed linear polarizers were oriented at 45° with the vertical capillary axis.
The thickness of the sample was l = 2.65 mm, so that 4th order magenta,
appearing at the interface near the end of this time series, implies a
Δn = 8.3 × 10^{-3}. (d) SAXS pattern collected from the sample imaged in (c) at a distance of
10 mm from the interface, at the end of the time series, and (e) just below the
interface.

Small-angle X-ray scattering and birefringence from evaporated samples
Whereas SAXS data from non-evaporated samples are isotropic, the data collected on samples from which evaporation has
occurred are anisotropic (see Fig. 2d and e). A spatio-temporal
plot of the evaporation process (Fig. 2c) shows birefringence that
grows from the evaporation interface towards the bulk, invading
the sample on macroscopic length scales on the order of cm in a
matter of weeks. Because the birefringence remains unchanged
when samples are rotated by an angle θ around their cylinder axis
c || z, the ordering must necessarily constitute a cylindrically
symmetric distribution of particle normals ̂n around this direction.
The successive changes of the birefringence colours
(determined by the retardation Δnl, with l being the sample
thickness) signal the existence of a long-lived gradient in either
the order (as characterized e.g. via the nematic order parameter
S2), in the concentration of particles (or equivalently the volume
fraction φ), or both (because Δn ∝ S2φ).17

We confirm the presence of a gradient in φ with X-ray
transmission, following previous work by Fonseca et al.23 From
this analysis, volume fractions around φ = 2% are obtained in
non-evaporated samples or in evaporated ones far away from the
interface, whereas close to the interface the volume fraction
gradually rises, reaching above φ = 6% in some cases. By con-
verting volume fraction data to particle concentrations, we find
that the concentration near the interface exceeds Cw = 9 wt%,
reaching well into the range in which Mourchid et al.16 have
observed textures reminiscent of nematic defects in Laponite
(LRD) dispersions, but where simulations yield arrested
dynamics without order.24 A significant structure factor contrib-
tion to the scattering signal accompanies the concentration
gradient, with correlation peaks becoming progressively more
pronounced as the concentration increases. Near the interface,
the maximum deviation from the calculated form factor occurs
around q = 0.57 nm^{-1} (Fig. 1b), roughly corresponding to
characteristic distances in real space of 2π/q = 11 nm. The peaks
share the anisotropy of the overall scattering patterns (see
Fig. 2e), and therefore likely represent a typical face-to-face
distance between approximately parallel platelets; for a given
center-center separation, this configuration minimizes the
repulsion between discs interacting via a purely repulsive
potential,31,32 and minimizes the excluded volume.

Calculating the order parameter
To assess whether a gradient in the order parameter S2 exists in
evaporated samples, we compare the anisotropy in the
measured SAXS data to simulated SAXS patterns computed with
a suitable orientational distribution.17,33,34 In our computations
we use a structure factor S(q) = 1 and Fournet’s expression35 for
the form factor of a cylindrical disc of height h and radius r to
approximate the form factor of a Laponite particle through

\[ F(q, r, h, r) = K \frac{\sin((qh \cos \gamma)/2)}{(qh \cos \gamma)/2} \frac{2J_1(qr \sin \gamma)}{qr \sin \gamma}. \]  

Here γ is the angle between the scattering vector ̂q and the
disc normal ̂n (see Fig. 3a) and J1 the first order Bessel function
of the first kind. For the orientational distribution of disc
normals we use the classical Maier–Saupe distribution36–38

\[ f(\theta, m) = C(m)\exp(m \cos^2 \theta). \]  

The function is normalized to one over half the unit sphere
because opposite orientations of ̂n correspond to identical
physical orientations of a platelet. The parameter m ≥ 0
determines the narrowness of the distribution of ̂n around z and
yields S2 as

\[ S_2(m) = 2\pi \int_0^{\pi/2} \left( \frac{3 \cos^2 \theta - 1}{2} \right) f(\theta, m) \sin \theta d\theta. \]  

We express the angle γ between ̂q and ̂n via θ and φ (which
fixes the orientation of ̂n in the lab frame) and α (which fixes the
direction of ̂q in the x, z-plane) so that trigonometry gives

\[ \gamma(\theta, \phi, \alpha) = \cos^{-1}(\sin \theta \cos \phi \cos \alpha + \cos \theta \sin \alpha). \]  

The q- and α-dependent intensity on the detector for a given
order as specified by m is then found by numerical integration
of the squared form factor weighted by the orientational
distribution. The integral is written as

\[ I(q, \alpha, \phi, h, r, m) = K^2 \int_0^{\pi/2} \int_0^{2\pi} \int_0^{\pi/2} \xi f(\theta, m) \sin \theta d\theta d\phi dr. \]
We compare the calculated SAXS patterns for different \( S_2 \) with the experimental data in the \( q \)-range where the structure factor is flat (\( S(q) = 1 \)). The fitting procedure (after the parameters \( r_1, r_2 \) and \( h \) were determined from the isotropic data) involves finding the \( m \)-parameter which produces a calculated pattern whose anisotropy most closely matches the experimentally measured anisotropy. From this analysis, we find that even our most anisotropic SAXS patterns measured correspond to relatively low values of the order parameter, \( S_2 \leq 0.21 \). This is in contrast to what was found by Lemaire \textit{et al}.\textsuperscript{17} for similarly sized Laponite B dispersions, where uniform order around \( S_2 = 0.55 \) was reported. We also find that the relationship between \( S_2 \) and \( \Phi \) (Fig. 4a) appears relatively well-defined within the uncertainty associated with our measurements, and that this relationship reproduces across the investigated samples. The observed order grows continuously from around zero and qualitatively follows \( \Phi \) in a manner reminiscent of the expected dependence of \( S_2 \) on \( \Phi \) for isotropic–nematic transitions in an ordering field,\textsuperscript{40–41} for which the free energy \( F \) may be expanded in powers of the order parameter so that

\[
F = F_0 + \sigma S_2 + c_2 S_2^2 + c_3 S_2^3 + c_4 S_2^4. \tag{9}
\]

Here \( F_0 \) is the reference energy for the isotropic system and \( \sigma \) the strength of the ordering field; \( c_2 \) and \( c_4 \) are parameters that change sufficiently slowly in the vicinity of the phase transition so that the prefactor \( c_2 = \beta (\Phi^* - \Phi)^2 \) is the only parameter which depends on \( \Phi \). By setting the partial derivative of the expansion to zero, the equilibrium value for \( S_2 \) follows from

\[
\frac{\partial F}{\partial S_2} = \sigma + 2c_2 S_2 + 3c_3 S_2^2 + 4c_4 S_2^3 = 0. \tag{10}
\]

We find that, assuming an underlying very weakly first order transition, we can fit our measurements for \( S_2 \) and \( \Phi \) with such a dependence (Fig. 4a). We however stress that the free energy minimization approach only applies if a shift in order away from the observed \( S_2 \) at any given \( \Phi \) drives the system upwards in the free energy landscape.

**Fig. 4**  
(a) Estimated order parameter \( S_2 \) versus the volume fraction of LRD particles \( \Phi \). The error bars represent the standard deviation on the mean of the volume fraction from several transmission measurements, and the different symbols represent data from a set of equivalently treated samples. The solid line shows the best fit of a function inspired by an extended Landau–de Gennes model to the data, as described in the text. (b) Birefringence image of a Laponite sample with air bubbles.
History dependent order

The origin of orientational order in Laponite (LRD) dispersions has been an unresolved issue in the literature. Mourchid et al. early on observed textures reminiscent of nematic defects in samples with significant viscoelasticity. A later study of oedometrically compressed samples with NMR found orientational order developing with the concentration in a manner similar to that found in our samples (Fig. 4a), albeit at higher salt concentrations. The compression study predicts perfect order at very high volume fractions; this is similar to what is predicted by the empirical fit to our data (Fig. 4a), where an order parameter of $S_2 = 1.0$ is achieved when $\Phi = 90\%$.

Well before such high volume fractions are reached however, we note that samples are prone to fracture, pointing to the evaporation process causing significant stresses on the glass. We also observe that implanted air bubbles which are spherical in the bulk (or near the interface prior to evaporation) become progressively more oblate towards the evaporating surface, with the unique, short axis of oblate bubbles pointing along the capillary axis $c \parallel z$ (see Fig. 4b). From the spatio-temporal birefringence data (Fig. 2c), we estimate that evaporation-induced compression of the colloidal structure causes an average normal rate of deformation of $4 \times 10^{-7} \text{s}^{-1}$; this value is two orders of magnitude larger than the inverse of the estimated structural relaxation time $1/(\tau_2) = 1 \times 10^{-9} \text{s}^{-1}$ from DLS (Fig. 1a). This implies that the response of $C_w = 3.0 \text{ wt}\%$ Laponite (LRD) dispersions to such strain rates is solid-like, i.e. is elastic or plastic. Plastic events, which involve irreversible displacements or reorientations in response to stress, are known to impart permanent anisotropies to e.g. simulated, sheared silica glasses. However, although such plastic events drive the system from less to more favoured configurations under stress, it is important to note that the order resulting from deformations is generally not intrinsic but history-dependent. Monte-Carlo simulations of highly charged platelets of the same size as Laponite (at ionic strengths comparable to our study) suggest that the density at the orientational order–disorder transition corresponds to $\Phi = 12\%$. This volume fraction is considerably higher than the range of volume fractions we explore, supporting the hypothesis that the weak orientational ordering seen in our experiments has a different origin than that which would arise spontaneously from excluded volume effects and electrostatic interactions.

4 Conclusions

Based on our observations, we conclude that the orientational order observed in our Laponite (LRD) samples results from plastic deformation of the colloidal glass in response to compression caused by evaporation. That the order nevertheless should follow the volume fraction is not unexpected since the evolution of both parameters within this picture follows the compression. One might imagine a situation where, despite the quite obviously slow translational dynamics, the rotational degrees of freedom associated with $\vec{n}$ were able to equilibrate. The slow decay of depolarized correlations in the DLS data argues against this possibility. We therefore conclude that the birefringence in our samples is due to plastic deformations driving the initially disordered glass into a state where a long-lived concentration gradient is accompanied by orientational order and increasingly pronounced interparticle correlations.

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