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Time-dependent Re-Aggregation of Colloidal Laponite Clay Suspensions

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Summary

We study a synthetic clay suspension of laponite by measuring transient electric birefringence (TEB) and dynamic light scattering (DLS) over time. Experiments show a strong dependence on stirring of the sample for anomalous TEB behaviour, consistent with the effect being caused by competing optical contributions from single clay platelets and aggregates. Stirring must take place shortly before measurements, as samples will in the order of days reach an equilibrium where the anomalous effect is only observable by double pulse TEB measurements. Shaking a sample again after it is measured, does not reproduce the same time evolution, sample reaches equilibrium earlier. DLS show aggregates increasing in size and ratio with regard to platelets, supporting the TEB measurements.

Vi studerer en kolloidal laponitt leire ved å måle transient elektrisk dobbeltbrytning og dynamisk lysspredning over tid. Forsøk viser en sterk avhengighet til risting av prøven på den anomale transiente dobbeltbrytningen, konsistent med at effekten er forårsaket av konkurrerende optiske bidrag fra leire enkeltplater og aggregerte partikler. Ristingen må ta plass kort tid før måling, da prøver vil nå en likevektstilstand hvor den anomale effekten kun kan måles med dobbelpuls transient elektrisk dobbeltbrytning. Riste prøven på nytt etter den er målt gjenskaper ikke den samme tidsutviklingen, prøven når likevektstilstanden tidligere. Dynamisk lyspredning viser at aggregatpartiklene øker i størrelse og signalforhold til enkeltplatene, som støtter transient elektrisk dobbeltbrytningsmålingene.

Preface

The following text is my master project work in Physics and Mathematics, Applied Physics, at the Norwegian University of Science and Technology. The work was carried out in the spring of 2014, at the Department of Physics. Project work concerned mainly the Transient Electrical Birefringence of laponite clay particles, and was a continuation of my semester project the preceding semester. During the course of performing the planned experiments, we stumbled upon an interesting effect of the laponite clay samples in the hours following the sample being shaken. Due to the interesting nature of our discovery, it was decided to push forward to attempt publication of our findings. The following text is therefore in the shape of a research article, laid out in the style prescribed by the American Physical Society for use in drafts and submissions, using their REVTeX LaTeX macro package.

TIME-DEPENDENT RE-AGGREGATION OF COLLOIDAL LAPONITE CLAY SUSPENSIONS

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Abstract

We study a synthetic clay suspension of laponite by measuring transient electric birefringence (TEB) and dynamic light scattering (DLS) over time. Experiments show a strong dependence on stirring of the sample for anomalous TEB behaviour, consistent with the effect being caused by competing optical contributions from single clay platelets and aggregates. Stirring must take place shortly before measurements, as samples will in the order of days reach an equilibrium where the anomalous effect is only observable by double pulse TEB measurements. Shaking a sample again after it is measured, does not reproduce the same time evolution, sample reaches equilibrium earlier. DLS show aggregates increasing in size and ratio with regard to platelets, supporting the TEB measurements.

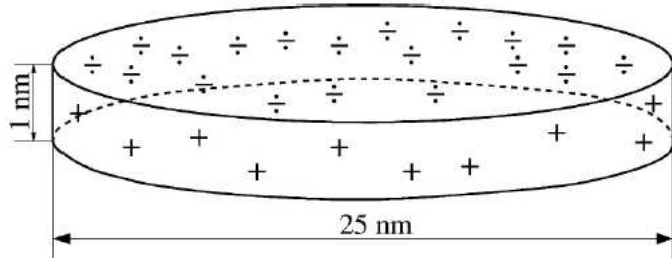


FIG. 1. Schematic illustration that shows the geometry and dimensions of a laponite clay platelet. Surface charges are indicated by + and ÷.

INTRODUCTION

Laponite is a synthetic clay, belonging to the smectite group of swelling clays. Dehydrated, the laponite platelets stack, due to the charge distribution along the surface of the platelet. [1, 2] Laponite is monodisperse in size, separating it from most other natural and synthetic clays. It has a diameter of 25 nm to 30 nm with a thickness of 1 nm, shown schematically in Fig. 1. This monodispersivity contributes to the fact that laponite is widely studied. In practical application, Laponite is used as a rheology modifier on among others; surface coatings, paints, ceramic glazes, and in nano-composite construction.

Laponite has a complex phase diagram, with phases including isotropic liquid, isotropic gel, nematic gel, and flocculation [1, 2]. We will in this study look at colloidal laponite clay in the isotropic liquid phase, which is a suspension of Brownian particles, with single platelets and larger aggregate particles. Samples are studied by dynamic light scattering (DLS) and transient electrical birefringence (TEB), after the samples have been shaken by an ultrasonic bath. Combining data from these two experimental techniques, we will attempt to explain some of how colloidal laponite clay develops after such a perturbation.

The so called anomalous transient electrical birefringence behaviour of colloidal clay, where the colloidal suspension has a change in refractive index along and normal to the applied field, have been studied and discussed in several previous works. Although discovered in 1939 [3], the effect is still researched, and no complete explanation has been found.[4-6]. In this study, we will look at how TEB changes with shaking of the sample, and how that relates to the understanding of how this anomalous behaviour arise.

TRANSIENT ELECTRIC BIREFRINGENCE

When no external forces influence the orientation of rigid particles in a solution, they will be randomly oriented and in thermodynamic equilibrium. Any specific orientation will relax back to random orientation through Brownian motion, rotational diffusion. This decay is a function of the rotational mobility tensor.

Birefringence is caused by phase difference δ between light polarised along different directions. With the incoming light propagating along the z-direction, birefringence is then the difference between the indices of refraction n_x and n_y

$$\delta = (k_y - k_x) \cdot l = \frac{2\pi}{\lambda} \Delta n \cdot l \quad (1)$$

where wave vector $k_i = n_i 2\pi/\lambda$. l is the path length of the light travelling through the sample. Generally in TEB measurements, the response of the sample is either along the electric field or normal to it. And the resulting TEB signal is dependent on one or more particles acting on the same n_i , giving a sum of exponential functions acting in the same direction.[7]

In colloidal clay TEB measurements, it has been shown that the resulting signal is consistent with two main competing exponential functions, meaning both n_i 's are affected, and the birefringence depends on $k_y - k_x$ instead of only one of them. When the decay time of these two contributions are not equal, we observe what is sometimes called the anomalous behaviour of colloidal clay TEB measurements. Due to the manner of detection, measured intensity $I(\tau) \propto \delta^2$, meaning the measured signal is the difference squared of k_y and k_x . These two main contributions are generally referred to as a primary positive signal, and a secondary negative signal. [6]

DYNAMIC LIGHT SCATTERING

In dynamic light scattering, the normalised intensity autocorrelation function $g^{(2)}(\tau)$ is measured. τ is in DLS the lag time of the correlated intensities $I(t)$ and $I(t + \tau)$. The field intensity autocorrelation function $g^{(1)}(\tau)$ is coupled to $g^{(2)}(\tau)$ by the Siegert relation

$$g^{(2)}(\tau) = 1 + [g^{(1)}(\tau)]^2. \quad (2)$$

In a polydisperse sample, the autocorrelation will depend on a distribution of decay rates, $G(\Gamma)$;

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma)e^{\Gamma\tau}d\Gamma \quad (3)$$

found by CONTIN analysis of the intensity autocorrelation. With a decay rate $\Gamma = D_t q^2$, where D_t is the translation diffusion coefficient and q the scattering vector, we can relate Γ to hydrodynamic radius r_t through the Stokes-Einstein relation

$$D_t = \frac{k_B T}{6\pi\eta r_t}. \quad (4)$$

k_B is the Boltzmann constant, T the temperature of the sample, and η the viscosity. A thorough treatment of DLS experiments can be found in Ref. [8]

EXPERIMENT

Sample preparation

Laponite RD powder purchased from BYK Additives, was added to deionised water. pH levels were not controlled. Samples were stirred for 30 min using a magnetic stirrer, before being filtered with a PALL Acrodisc 1.2 μm Versapor syringe filter. All samples studied were 0.5% laponite by weight. Weight of filtered laponite was assumed to be negligible. Samples were then stored in sealed glass containers. Sample portions were taken out and shaken in an ultrasonic bath before measurements. Ultrasonic bath used were a VWR symphony ultrasonic cleaner, and samples were shaken for 10 min at power setting 8. At time of measurement, samples were 2-3 months old. Ultrasonic bath were used for consistency and reproducibility, but the effect of shaking was still clear and measurable after < 5 minute manual shaking.

Laponite suspensions are known to undergo an ageing process over long time, particularly when exposed to air.[9, 10] No other measures were taken to compensate for this, than to seal the samples when stored.

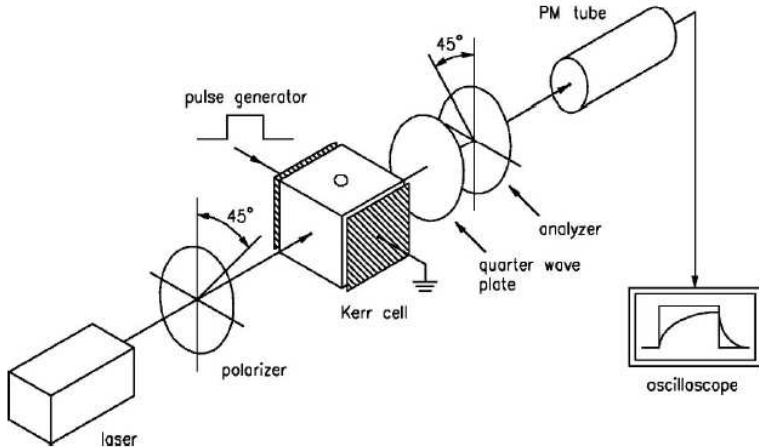


FIG. 2. Schematic illustration of the TEB setup.

TEB setup

Experimental setup for TEB measurement are shown in Fig. 2. The light source is an argon-ion laser (Stellar-Pro Modu-laser) operating at wavelength 488 nm. The light is monochromatic and linearly polarised, 45° relative to the electric field in the Kerr cell. The Kerr cell contains the sample, and exposes it to a horizontal pulsed electric field. There is 3 mm between the parallel electrodes. The electric field induces a transient optical anisotropy, that results in elliptically polarised light exiting the cell.

With polariser and analyser perpendicular to each other, the light intensity measured by the photomultiplier (PM-tube) is proportional to the square of the the birefringence Δn , resulting in quadratic detection. The signal from the PM-tube is captured by a Tektronix TDS 694C 3GHz digital storage oscilloscope, and exported to a computer.

The temperature of the sample were not controlled, and is assumed to be 21°C . Samples were stored at 21°C , in the lab where experiments were performed. With one $600\ \mu\text{s}$ pulse at $213\ \text{V mm}^{-1}$ an hour, any heating from the electric pulses is assumed to be negligible. [1]

Further Technical details can be found in Ref. [11–13]

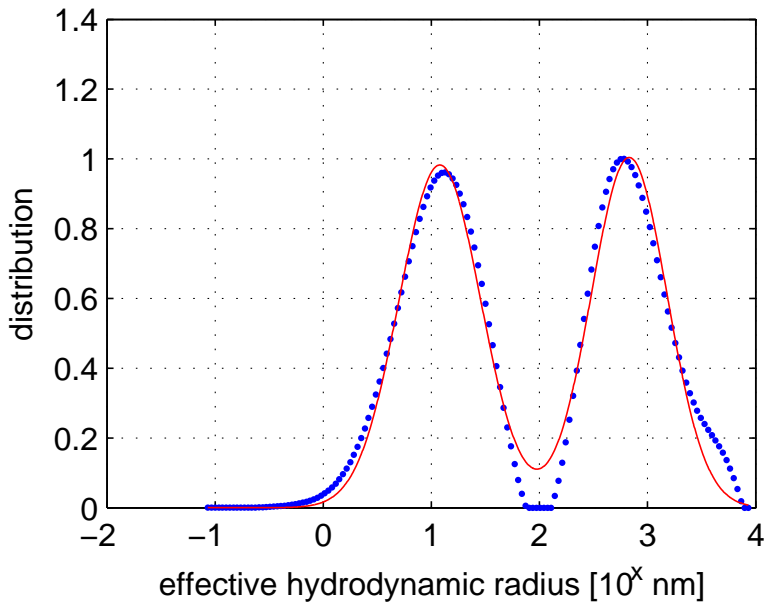


FIG. 3. Distribution of hydrodynamic radii for a laponite sample $t = 0$ hours after shaking. Solid line is a Gaussian least-squares fit over the two peaks.

DLS setup

DLS measurements are performed on standard equipment, with a laser beam hitting the sample, and scattered light being detected at an angle θ off the beam path. The light source is a vertical linearly polarised He-Ne laser with wavelength 633 nm. Signal is interpreted by an ALV/LSE-5004 Digital Correlator, and a CONTIN fit is performed on the resulting intensity correlation function by the ALV correlator software, resulting in a decay time distribution.[8] Sample is temperature controlled, and for this measurement at 23.8°C. All measurements were done at angle $\theta = 90^\circ$, and the viscosity of the sample is assumed to be that of water.

DISCUSSION

In Fig.3 the computed radial distribution for a single measurement is plotted, as well as the fit to obtain particle radius and relative scattering intensity. Measurement was taken

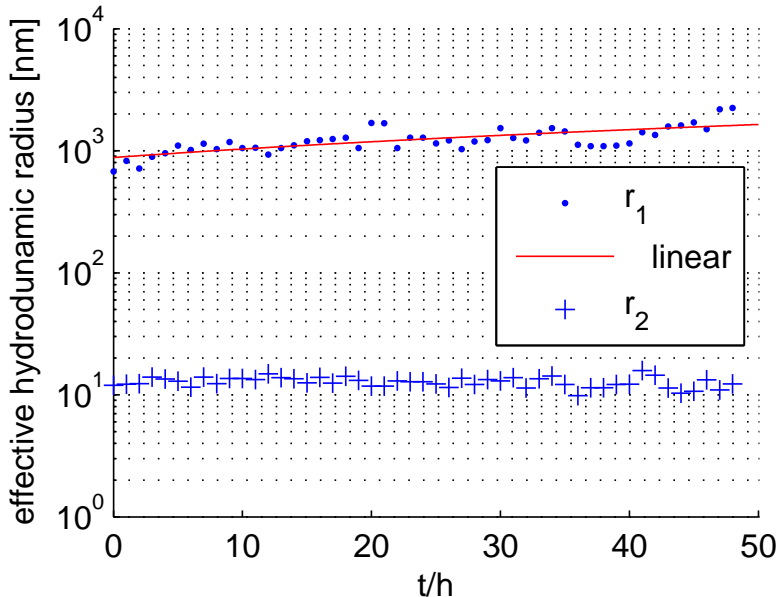


FIG. 4. Fitted radii for each hour of DLS measurement.

over 5 min, and one such measurement was done an hour for 48 hours. The fit performed is a Gaussian least-squares fit. We obtain two distinct peaks for hydrodynamic radius. These are at $t_{\text{met}} = 0$ after shaking approx. 12 and 680 nm. They are assumed to be from single platelets and aggregate particles, respectively.

Fitted radii for the entire measurement duration is plotted in Fig. 4. Radius r_2 appears constant for the entire duration, as would be expected from a signal resulting from single platelets. For the aggregate peak, r_1 increases for the entire measurement duration. r_1 is plotted with a linear least-squares fit. From this we can assume that the aggregate particles increase in size over time, after the initial ultrasonic shaking at time $t=0$.

The ratio between the r_1 and r_2 peaks is plotted for the entire measurement in Fig. 5, with a linear least-squares fit. Ratio of aggregate peak compared to platelet peak A_1/A_2 increases. This indicates that the scattered intensity from aggregate particles increase relative to the scattered intensity from platelets. Such a development is consistent with single platelets being absorbed by aggregate particles, and they consequently increasing in size.

Fig. 6 shows a single double pulse TEB measurement of the Laponite sample, at time $t = 0$ h. An electric field square double pulse begins at $\tau = 0$, changes direction from \vec{E} to

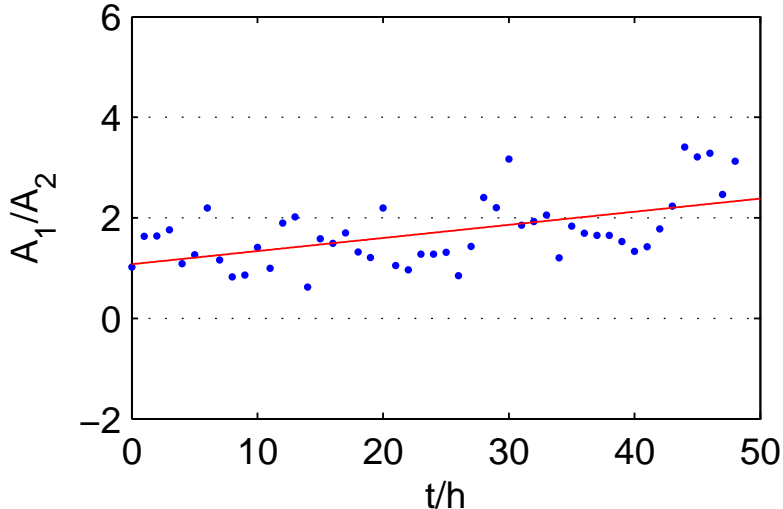


FIG. 5. Ratio of DLS signal distribution amplitudes A_1 and A_2 between the aggregate and platelet peaks. The aggregate peak grows increasingly dominant.

$-\vec{E}$ at $\tau = 300 \mu\text{s}$ and ends at $\tau = 600 \mu\text{s}$. Field strength E is 213 V mm^{-1} . Pulse length and strength is constant for all measurements performed here.

This TEB measurement shows several features characteristic of the anomalous TEB response of colloidal clay. In the first region, $\tau = 0 - 300 \mu\text{s}$, we see the almost instantaneous build up of the signal, followed by a slower decay, reaching an equilibrium by $\tau = 300 \mu\text{s}$. This is caused by the two main competing TEB signals, being summed and squared due to the way the experimental TEB setup detects change in birefringence.

Immediately after field direction change, we observe a peak in the signal, followed by a decay back to the previous equilibrium. In TEB measurements, contribution from induced dipoles will almost instantaneously change with the electric field, by change in electron charge density. It is thus virtually impossible to detect any discontinuity in the TEB signal. Intrinsic dipoles will turn with the signal, and contribution will be temporarily suppressed, as the particles turn 180° . What we observe in colloidal clay TEB measurements is that we suppress one signal, while the other continues unaffected. This gives rise to a peak or valley, depending on the relative strength of the signals.

The anomalous effect sometimes found after the pulse has ended, is not observed here. It

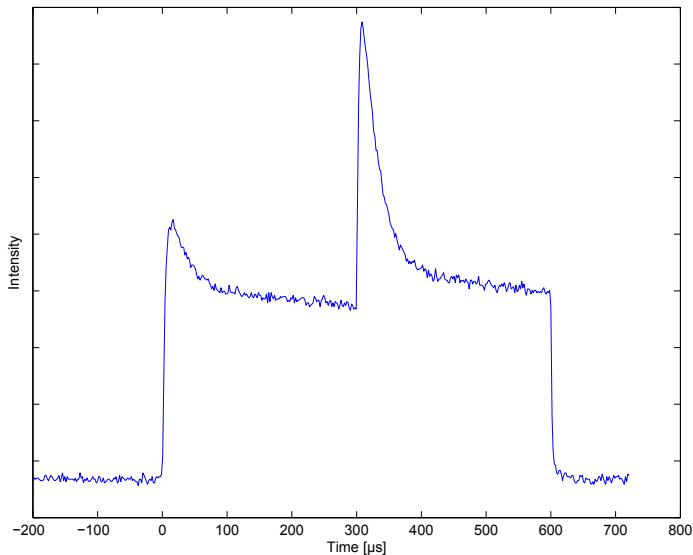


FIG. 6. Measured TEB signal for a laponite sample $t = 0$ hours after shaking. Curve shows the competing fast and slow responding signals, as well as the suppression of the slow signal at field reversal, at time = $300 \mu\text{s}$ into the pulse.

will under certain configurations show as a dip to zero, before building up to a local maximum, and decaying. It is dependent on the negative, slow decaying signal being dominant at the time of field cut off.

Similar to the DLS measurement, Fig. 7 shows the evolution of the sample 48 hours following ultrasonic shaking. Each line represents a single measurement, and the lines are two hours apart. Electric field commences at $\tau = 0 \mu\text{s}$, changes direction at $\tau = 300 \mu\text{s}$, and ends at $\tau = 600 \mu\text{s}$, as before. We observe the same sharp rise as discussed for Fig. 6 for approx. the first 20 hours. the following hours, the positive fast signal appears to vanish, and we have only a slow rising negative signal.

In the region immediately following the field direction change, we see that the peak caused by suppression of the intrinsic dipole signal increases over the first 20 hours, before sharply dropping off. In the long time frame limit, $t < 40$ hours, the peak is now a valley, indicating that the signals have changed from the positive fast signal being larger, to the negative slow signal being larger. Double pulse measurement is now the only way to observe that the

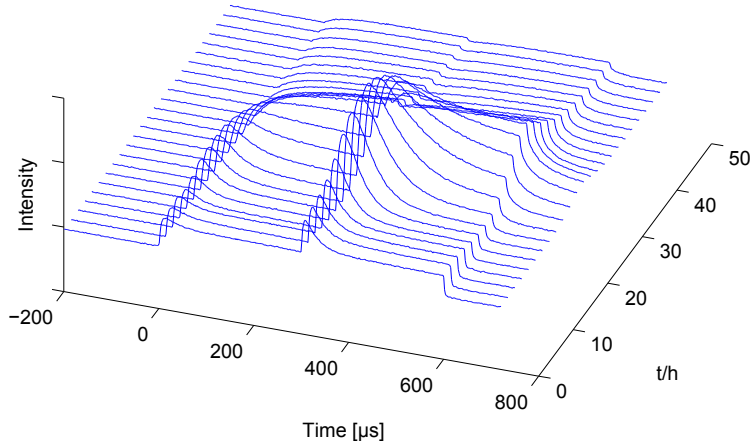


FIG. 7. TEB measurement of a laponite sample 48 hours after shaking.

sample still shows an anomalous effect. This may explain instances where TEB measurement of colloidal clay samples have not exhibited an anomalous effect.

The measurements taken over two days, with sample shaken after the first 24 hours, are shown in Figs. 8 and 9. Each line represents one measurement, and the lines are 1 hour apart. If the time after shaking were the only factor governing the development of the sample within our experimental time frame of two days, we would expect the shaking process to reset the sample to its initial state at day 1 time $t = 0$ h. The two 24 hour measurements should then be identical. They are not, although they follow the same general progression.

The sample on day 2 appears to reach long time limit equilibrium faster, with the field change peak reaching a maximum at approx. $t = 9$ h, compared to the day 1 and the 48 hour measurements, where the peak lies around 16-24 hours. Furthermore, the day 2 measurement reaches peak inversion already at 24 hours, while for the 48 hour measurement, this happens at approx. 36 hours.

Peak values for the day 1 measurement are truncated, due to incorrect calibration of the measuring equipment. The day 1 measurement is consistent with the 48 hour measurement, and is expected to have had progressed similarly, as the experiment was performed in an

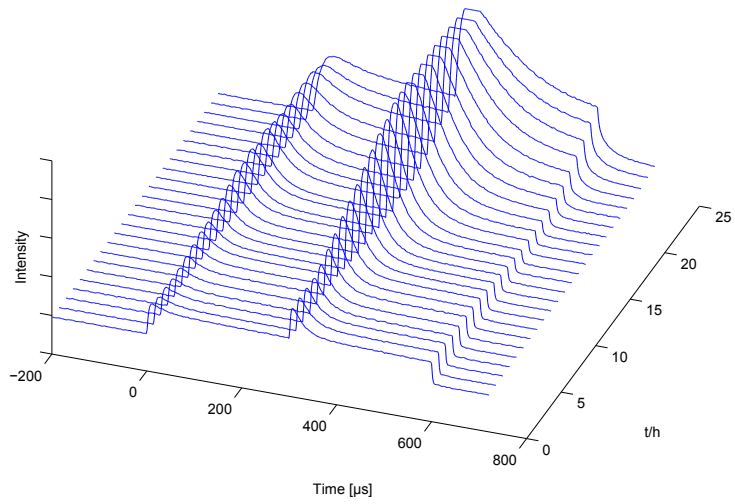


FIG. 8. TEB measurement of laponite sample 24 hours following shaking.

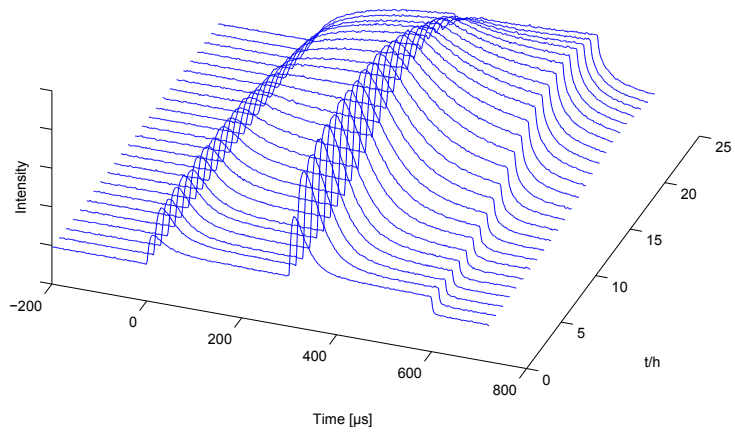


FIG. 9. TEB measurement of the same sample as Fig. 8, extracted and shaken again.

identical manner.

SUMMARY AND CONCLUSION

We study the change in a laponite clay suspension after it has undergone a ultrasonic shaking, by DLS and TEB measurements. This is to the authors knowledge the first time the time-dependent change after shaking of the sample has been studied.

Both DLS and TEB show a development in the hours following the sample shaking. With DLS we see that the sample contains two main particle sizes, one steady at hydrodynamic radius of $r_2 = 13$ nm, the other at $r_1 = 700$ nm and increasing to > 1000 nm over the following 48 hours. The ratio of amplitudes between aggregate and platelet signal were also increasing, indicating that aggregate particles absorbed platelets over time. TEB showed a similar development, where the signal contribution from aggregate particles grew increasingly dominant over time.

The insight provided into how colloidal clay develops after such a perturbation is important not only for further studies into aggregation, but also further TEB studies, as the TEB signal measured here is highly dependent on time since sample was disturbed. A sample prepared at the start of a workday, will at the end of the same day show a different response.

Samples were not prepared in the manner suggested by Ruzicka and Zaccarelli [2], and long term changes to the sample were not compensated for. Samples were filtered and stored in sealed containers, but initial stirring by magnetic stirrer were not as long, and samples were not prepared in a CO₂ free atmosphere.

In future studies it would be important to prepare the sample in accordance with the guidelines given by Ref. [2]. Other sample concentrations could be studied, as well as experimenting with the power and length of the shaking process. Specifically to see whether the radius of the aggregate particle measured with DLS would start at a lower initial value, and whether sample shaking in the TEB measurement would fully reset the sample to the way it behaved the previous day. DLS measurements of the same reset would be useful in comparing to TEB. Performing TEB decay measurements to determine rotational diffusion and hydrodynamic radius would also be interesting, to look at the same time evolution.

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Appendix

Photomultiplier linearity

As colloidal clay suspensions are strongly responding material in transient electrical birefringence experiments, it was necessary to ensure that the transmitted light were not beyond the operational range of the measurement photomultiplier tube. By rotating the analyser of the experimental TEB setup a fixed step, and plotting the measured intensity as a function of the square of this step, we get a result that should be linear as long as the PM-tube is not overloaded.

The result of this test is shown in Fig. 1. Several configurations were tried, and the one shown is that which gives us the greatest working range. All TEB measurements performed here are set up, through optical filters and laser power settings, to stay within the approximately linear region of PM-tube response (y -axis) of less than "80".

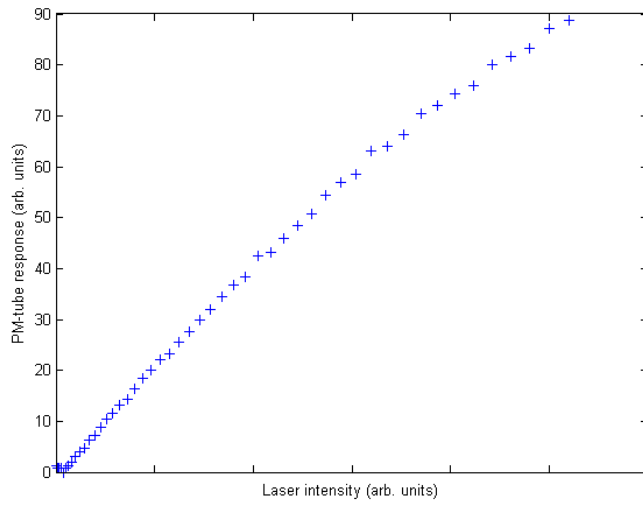


Figure 1: Measured signal of the photomultiplier-tube against a linear increase in laser intensity.