

Acknowledgement

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Summary

This diploma thesis is primarily an experimental study of the clay sodium fluorohectorite based on dynamic light scattering experiments. The method used is a homodyne single light scattering method, where we look at the fluctuations of the intensity of light scattered from the clay suspension. The experiments are restricted to an analysis of a 2,9 w/w % sample of sodium fluorohectorite dissolved in a 2E-3M sodium chloride and distilled water solvent. The suspension is phase separated in three distinguishable phases. The light intensity autocorrelation function for light scattered 90° is found for all the different levels of the clay suspension and the properties of this correlation function are analysed in order to say something about the size of the clay particles. Light scattering from complex systems, as the clay suspension indeed is, is not at all trivial, and the theoretical background for the analysis is featured by assumptions which do reduce the possibilities of drawing accurate conclusions. An obvious improvement for a further analysis would be the possibility to tune the scattering vector in order to study its influence of the correlation function, for instance by using a goniometer.

Based on the correlation data we may however assume that the mean size of the clay clusters in the uppermost phase of the suspension is limited to be bigger than approx. 100nm.

The work required to get familiar with the experiments, acquire the data presented and none the less analyse the data within the total time limit of four months exceeds the limits of this thesis, hence this report must be regarded as a fundament for further analysis. The conclusion in this report will in that respect just be treated as possible valid conclusions.

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1 Introduction

1.1 Motivation

The clay as a material is known for several thousands of years. Dried clay in ceramics is found from different prehistorical cultures throughout the world. Despite this long history of clay, the structure and dynamics of the clay and clay suspensions are far from well known. The properties of clay suspension is strong influenced by the existence of free ions in the suspension. A single suspension may go from a pure liquid phase through a gel phase and further flocculate and transform into a solid form just by adding small amounts of salt.

The scientific work on observing different phases in clay suspensions was started in 1938 when I.Langmuir observed a macroscopic phase transition in natural clay gels [1]. This was the start of many observations on clay systems, though theoretical expressions was hard to find. A remarkable and frontier breaking work was however done by L.Onsager when he proved the existence of a nematic gel phase in a system of two dimensional hard disks, which is case for the clay [2].

The clay *sodium fluorohectorite* has shown some nice phase separations in previous work [7] but the properties of the clay particles in these phases is still not known. The task of this thesis is hence to collect light scattering data from this clay suspension and if possible, say something about the size of the particles.

1.2 The diploma work

This report summarize an experimental work on investigating a sodium fluorohectorite phase separated suspension by the use of dynamic light scattering (DLS). The idea was to collect the correlation function for different levels in a clay sample in order to identify size properties of clay suspension. Since phase transitions are observed in the clay sodium fluorohectorite, it is likely to believe that the size of the clay clusters in the suspension change as we go down in the sample. A challenge was to get small volumes out of the original samples to study every level of the sample separately. This was necessary, since we had to dilute the samples in order to insure single light scattering. The phases at the bottom of the sample was not transparent at all, and the light scattered directly from these levels was most probably multiple scattered. An understanding of the theory for single light scattering is challenging enough for the limits of a diploma thesis.

Another experiment, which have been a part of this diploma thesis, was the collecting of correlation data directly from different sodium fluorohectorite samples. These samples have different concentration of sodium chloride added and was made during my project work [7]. The correlation data was collected from the different levels of the sample by sending the laser beam at the desired level of the sample and detecting the intensity fluctuations from this level.

The data from these experiments is not analysed properly through this report, and is only occasionally mentioned in the result chapter. The complete analysis of these data require a understanding of multiple light scattering as well as single light scattering, hence the data collected must preliminary only be recognized as raw data.

2 Theory

2.1 The clay and clay suspensions

The clay particles are basically charged platelets with a phyllosyllicate internal structure [3,4] and the principle shape is shown in Figure 2–1. The phyllosyllicate structure is originally uncharged, but when atoms inside the structure is replaced by atoms with another valance, the total clay particle may be charged. For the clay studied in this report, fluorohectorite, the charge per unit cell is $1.2 e^-$ [5]. To compensate for the net charge in the clay platelets, some

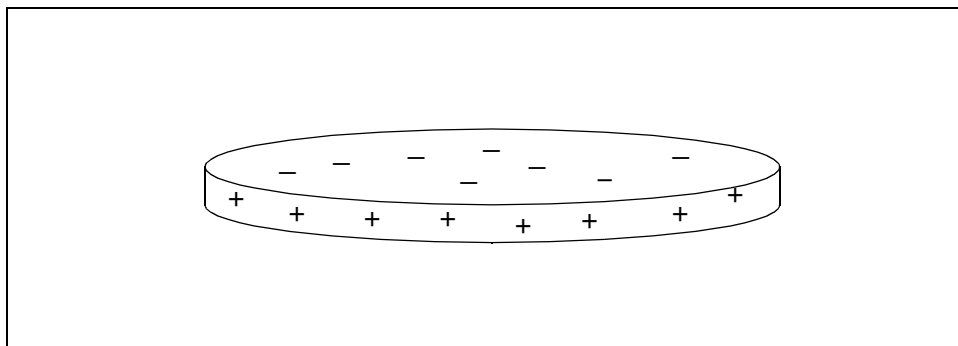


Figure 2–1: The clay platelet is the basic particle of the clay suspension. The surface is negatively charged because some Si atoms in the structure is replaced with metal atoms with lower valence. The surface thus adsorb free metal ions in the solvent surrounding the clay platelet to neutralize the charge.

sort of positive charge has to be adsorbed on the surface of the particle. In our case sodium ions are creating a positively charged atmosphere around the platelet and make the overall clay particle neutral. The clay studied in this thesis work is hence called sodium fluorohectorite. These ions are easy changeable with other ions and a variety of different fluorohectorite clays can be made.

The basic clay particles are because of their charge distribution repulsive, and when resolving dried clay powder in water, the particles may move freely around as single platelets. The addition of free counterions in the clay suspension, change however this. The clay suspension starts to phase separate, and after a while we can distinguish several separate phases [7]. How the interaction between basic clay platelets are changing while adding salt to the suspension is not a topic of this report, but the effect is related to the screening length for the clay particles when adding ions [12]. The more ions apparent in the solvent, the less thermal energy is needed before two platelets are coupled to each other. We can simply say that counter ions in the solvent oppositely charged to the clay, shield the electric field outside the particle. The clay platelets are then able to get closer before they see each other, and even get at a distance where they react and become one particle.

2.2 Light scattering

2.2.1 Quasi-elastic, homodyne light scattering.

In the experiment described later on the basic concept is that light is scattered when photons are scattered against atoms or molecules when passing through a material. When the photon is scattered small amounts of energy transfers from the photon to the material. In the light scattering experiment proceeding the loss in energy for one photon are considered very small compared to the total photon energy and hence the wavelength for the incident and scattered wave are assumed approximately equal [3]. The scattering vector is defined as

$$\Delta \mathbf{k} = \mathbf{k}_{sc} - \mathbf{k}_{in} = \mathbf{q}. \quad [2.1]$$

For quasi-elastic light scattering (QELS) the energy and by that the wave vector is approx. preserved and hence we have $|\mathbf{k}_{sc}| \approx |\mathbf{k}_{in}| = |\mathbf{k}| = k = 2\pi/\lambda$.

The experimental technique is further on characterized as homodyne light scattering, which refers to a detection of the fluctuations of the scattered light intensity itself. On the other hand we have heterodyne scattering, where the electrical field from the scattered light is mixed with a fraction of the field from the direct beam. The homodyne technique is sensitive only for relative motions in the scattering volume. Net transport of particles for instance in the mean of a liquid flow is not detected.

2.2.2 Brownian motions

Light scattering experiments has been widely developed to investigate the properties of physical systems such as size distributions, cluster structures etc. In a suspension where the particles motion is governed by a complex interacting system, the theory becomes very complicated and non-trivial, thus this chapter will only concern some simple ideal systems.

A simple first approximation is to assume that the particles are hard non-interacting spheres of equal size, which undergoes a random walk or Brownian motion. When a particle have been through many steps the probability for the particle to be at a position $\mathbf{r}$ from the original position at the initial time is well known and described by [18]

$$P(\mathbf{r}, t | 0, 0) = (4\pi Dt)^{-3/2} \exp\left(-\frac{r^2}{4Dt}\right). \quad [2.2]$$

The temporal evolution of $P(\mathbf{r}, t | 0, 0)$ is given by the parameter D , which is called the diffusion constant. This constant is actually describing the statistical motion of this system and is of great importance for the experiments described in this report. For the case where the particles are spherical with a radius of $2a$ the constant is given as [10]

$$D = k_B T / 6\pi\eta a \quad , \quad [2.3]$$

where k_B is the Boltzmann's constant, T the temperature and η is the absolute viscosity of the hydrodynamic system. The viscosity is given by the solvent and we require the brownian particles to be much larger than the particles of the solvent.

2.2.3 The mathematical correlation function

Mathematically the correlation function is defined as the averaging [8]

$$G(\tau) = \langle I(t)J(t + \tau) \rangle , \quad [2.4]$$

and is computed as

$$G(\tau) = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T I(t)J(t + \tau) dt . \quad [2.5]$$

$I(t)$ and $J(t)$ are signals dependent of t . $G(\tau)$ is called the auto correlation function or cross-correlation function depending on whether $I(t)$ and $J(t)$ are the same or different signals. In our case they are both the same signal. Additionally, the signal is for the most experimental purposes a discrete sample of the physical signal. For this case the correlation function is replaced by a sum

$$G(l) = \sum_{n=-\infty}^{\infty} x(n)y(n+l) , \quad [2.6]$$

and is the autocorrelation function if $x(n) = y(n)$.

2.2.4 Autocorrelation function for scattered light

An important assumption for the theory presented in this report is that the incoming light beam is a monochromatic plane wave. Let this incident light be described as $E_0 \exp[i(\mathbf{k}_0 \mathbf{r} - \omega_0 t)]$, where $\mathbf{k}_0$ is the incident wave vector and ω_0 are the angular frequency of the wave. The detector in a distance $\mathbf{R}$, far from the scattering volume is then observing a sum of the field radiated from each of the scattering particles, represented as [18]

$$E(t) = \sum_{j=1}^N E_j(t) = \sum_{j=1}^N E_0 \exp[i\phi_j(t) - i\omega_0 t] . \quad [2.7]$$

The information of the j th particle's position is covered in the phase $\phi_j(t)$ and is described by $2\pi/\lambda$ times the path length difference between the particle j and the origin position. The geom-

etry of the light scattered from a particle at $\mathbf{r}_j$ is shown in Figure 2–2. We can see that the phase

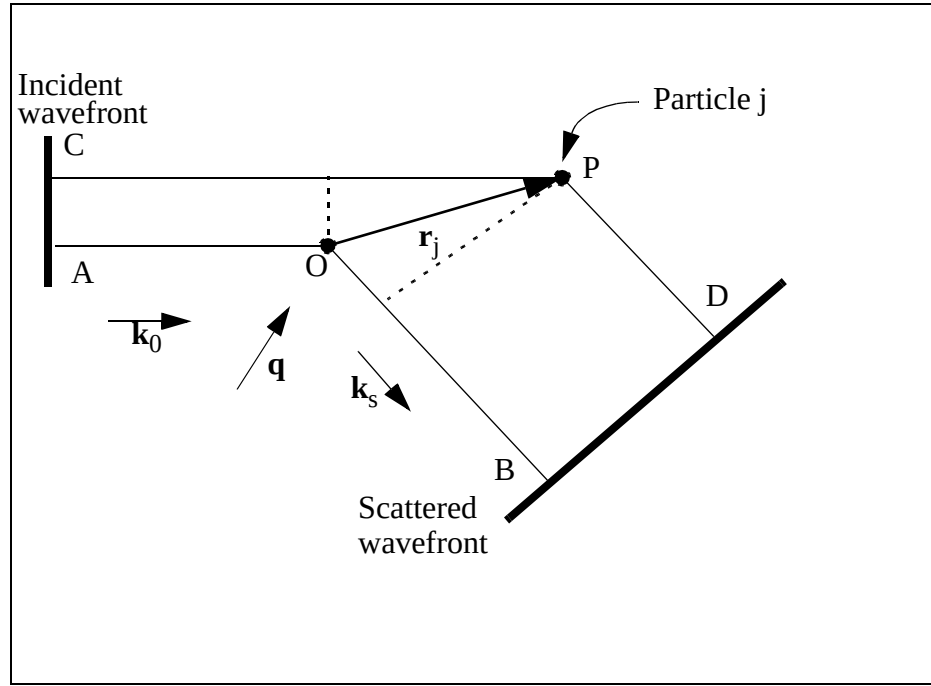


Figure 2–2: The figure shows how the geometry for light scattered by particle j is and how this influence the path length distance between the particle j and a scattering particle in origo. The scattering vector is also present and denoted as $\mathbf{q}$.

is

$$\varphi_j(t) = (2\pi/\lambda)(CPD - AOB) = \mathbf{k}_0 \mathbf{r}_j - \mathbf{k}_s \mathbf{r}_j \quad [2.8]$$

$$\varphi_j(t) = (\mathbf{k}_0 - \mathbf{k}_s) \mathbf{r}_j. \quad [2.9]$$

From Eq. 2.9 one can conveniently define a scattering vector $\mathbf{q}$ which is the difference between the incident wave vector and the scattered one

$$\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_s. \quad [2.10]$$

The magnitude of this scattering vector is given as

$$q = 2k_0 \sin \frac{1}{2}\theta = \frac{4\pi}{\lambda/n} \sin \frac{1}{2}\theta, \quad [2.11]$$

where θ is the angle between the incident wave vector and scattered wave vector, and n is the refraction index of the suspension. By use of the definition from Eq. 2.11 the phase of the scattering particle is written as

$$\varphi_j = \mathbf{q} \cdot \mathbf{r}_j. \quad [2.12]$$

Note that the phase of the scattered light only changes when particles are moving along the direction of the $\mathbf{q}$ vector. This implies as we will see later that the correlation function also react only to motion along the scattering vector. As we can see the phase of the light scattered from one particle is changed by 2π when the particle has moved a distance $\Delta r_j = 2\pi/q$ along the direction of $\mathbf{q}$.

As described on page 5 the correlation function is the property $\langle I(t) I(t+\tau) \rangle$ of a physical measurement $I(t)$. In this case the signal is the intensity signal from the scattered light $I(t)$, and the intensity is given as $I(t) = \beta E^*(t) E(t)$. The correlation function for the intensity, G_2 , is then given as

$$G_2(\tau) = \beta^2 \langle |E(t)|^2 |E(t+\tau)|^2 \rangle, \quad [2.13]$$

or by using Eq. 2.7

$$G_2(\tau) = |E_0|^4 \beta^2 \times \left\langle \sum_j \sum_k \sum_l \sum_m \exp[i(\varphi_j(t) - \varphi_k(t))] \exp[i(\varphi_l(t+\tau) - \varphi_m(t+\tau))] \right\rangle \quad [2.14]$$

As assumed the particles are moving around in a non-interacting regime, thus the particles positions are statistically independent. This gives rise to some simplification in the summing in Eq. 2.14. All the sums where one of the indices j, k, l and m are different from the other ones are all zero. Thus there is only contribution from the terms where at two and two indices or all four indices are equal. First of all we have a simple result when $j=k$ and $l=m$, which makes the exponentials equal to unity. Totally a number of N^2 contributions. The second possibility is when $j=m$ and $k=l$ but $j \neq k$, which gives $(N^2 - N)$ terms of the form

$$\langle \exp[i(\varphi_1(t) - \varphi_1(t+\tau))] \times \exp[i(\varphi_2(t) - \varphi_2(t+\tau))] \rangle. \quad [2.15]$$

The last situation is when $j=l$ and $k=m$ but $j \neq k$, which gives

$$-\langle \exp[i(\varphi_1(t) + \varphi_1(t+\tau))] \times \exp[i(\varphi_2(t) + \varphi_2(t+\tau))] \rangle. \quad [2.16]$$

All the terms like the one in Eq. 2.16 are equal to zero since we already have assumed that the particles are mutually uncorrelated, and will vanish.

Finally we are now able to compute an expression for the correlation function G_2 by using the previous terms. To make it more simple we assume that there is a great number of scattering particles in the scattering volume making $(N^2 - N) \approx N^2$. All the particles are still independent of each other which yields the expression

$$G_2(\tau) = N^2 |E_0|^4 \beta^2 \times (1 + |\langle \exp[i(\varphi(t) - \varphi(t + \tau))] \rangle|^2). \quad [2.17]$$

Now we have to evaluate the time averaging of the exponential function. The averaging is equivalent with taking the integral over the exponential function times the conditional probability distribution described by Eq. 2.2. Additionally by use of Eq. 2.9 and Eq. 2.10 on page 6 the averaging becomes [18]

$$\langle \exp[i\mathbf{q}(\mathbf{r}(t) - \mathbf{r}(t + \tau))] \rangle = \int_{-\infty}^{\infty} P(\mathbf{r}, t | 0, 0) \exp(i(2\mathbf{q} \cdot \Delta\mathbf{r})) d^3\Delta\mathbf{r}, \quad [2.18]$$

By obtaining Eq. 2.18 we see that the correlation function for Brownian particles are as follow

$$G_2(\tau) = N^2 |E_0|^4 \beta^2 [1 + \exp\{-(2D\mathbf{q}^2 \cdot \tau)\}]. \quad [2.19]$$

The correlation function is in the matter of monodisperse Brownian particles a sum of a constant term, representing the averaged intensity, and an exponential decay. The information of the size of the particles is then given from the dynamic part of the correlation function, namely the decay time since this decay is given by the diffusion constant and through Eq. 2.3 directly proportional to the particle size.

2.2.5 Rotational contribution to the correlation function

In the previous section correlation was related to particles moving in straight translation manner and where the particles did not interact. When the particles are of a size larger than the wave length of the light, λ , it is however possible that internal variations of the dielectric properties will cause variation in light scattered from different parts of the particle. We would then be able to detect internal structures in a single particle or cluster. The internal structure will, by use of some theoretical considerations, be visualized through the autocorrelation function so let us study the effect of rotational motions [9,10].

First of all the complete understanding of the theory demands a thorough investigation of the equations and the origin of these equations, and this report will just bring forth the most important equations to be able to see the final result. For the interested reader I will strongly recommend an article from Lindsay et al.[13] This article describes the theory in a very educational way and is the background for the theory proceeding in this report.

The translation motion cause the scattered light from each particle to travel different distances dependent of where all the particles are situated in the space as described in the previous section. This demands at least two particles, since the only way to achieve interference is when two rays of light travel different path length. In the matter of particles with internal structure the path length may vary when only one particle is present since scattering sub-volumes of the particle will give different path lengths dependent of the orientation of the cluster. This is however only possible if the size of the cluster is larger then one wavelength of the scattering vector. This constraint may as well be written as

$$qR_g \gg 1, \quad [2.20]$$

where q is the length of scattering vector and R_g is the radius of gyration of the cluster.

We start with a scattering volume with N clusters where n_α represents the number of scattering sub-particles in the α th cluster. The scattering field is then given by

$$\mathbf{E}_s(q, t) = E_0 \sum_{\alpha=1}^N \sum_{j=1}^{n_\alpha} \mathbf{P}_j^\alpha \exp[i\mathbf{q}\mathbf{r}_j^\alpha(t)], \quad [2.21]$$

where $\mathbf{q}$ is the scattering vector, $\mathbf{r}_j^\alpha$ is the position of the j th particle in the α th cluster at time t and $\mathbf{P}_j^\alpha$ is the polarizability of sub-particle j of cluster number α . To simplify the computation we restrict the theory to look at scattered light with the same polarization direction as the incident light and set $|\mathbf{P}_j^\alpha|$ equal to 1. We also assume that all the sub-volumes of the cluster are identical scattering spheres and set E_0 to one. The scaling of the correlation function is instead carried out at the end. We now try to find the intensity autocorrelation function G_2 as

$$G_2 = \langle |\mathbf{E}_s(q, t)|^2 |\mathbf{E}_s(q, 0)|^2 \rangle = \sum_{\alpha, \beta, \gamma} \sum_{j, k, l, m} \langle \exp[i\mathbf{q}(-\mathbf{r}_j^\alpha(t) + \mathbf{r}_k^\beta(t) - \mathbf{r}_l^\gamma(0) + \mathbf{r}_m^\delta(0))] \rangle \quad [2.22]$$

Decomposing the position of the i th particle in the α th cluster in terms of a position of the centre of mass of the cluster, $\mathbf{R}_\alpha(t)$, and the displacement of the i th particle from the centre of mass of the single cluster, $\mathbf{b}_i^\alpha(t)$, gives

$$\mathbf{r}_i^\alpha(t) = \mathbf{R}_\alpha(t) + \mathbf{b}_i^\alpha(t), \quad [2.23]$$

and we can then write the autocorrelation function as

$$G_2(q, t) = \sum_{\alpha, \beta, \gamma} \sum_{j, k, l, m} \langle \exp[i\mathbf{k}(-\mathbf{R}_\alpha(t) + \mathbf{R}_\beta(t) - \mathbf{R}_\gamma(0) + \mathbf{R}_\delta(0))] \rangle \times \exp[i\mathbf{k}(-\mathbf{b}_j^\alpha(t) + \mathbf{b}_k^\beta(t) - \mathbf{b}_l^\gamma(0) + \mathbf{b}_m^\delta(0))] \rangle \quad [2.24]$$

Since the different clusters are statistically independent, the contributions from most of the combinations of indices vanishes, since two and two of the cluster indices has to be equal («Brownian motions» on page 4). The first contributing combination is when $\alpha=\beta, j=k, \gamma=\delta, l=m$ and $\alpha \neq \gamma$. This gives just the constant average scattering intensity since all the exponentials in Eq. 2.24 become equal to one. This constant term, G_2^B , does not give any dynamic infor-

mation of the system because of its independency of time, and may be subtracted from the data before any analysis.

To achieve any dynamic data we require from now that $\alpha=\gamma$, which also implies that $\beta=\delta$. Now there are two possibilities which give rise to contributions. If $\alpha=\beta$ we are looking at a single cluster, and the correlation function is hence just related to rotation. The other case, when $\alpha\neq\beta$, there are two distinct clusters involved. In this case both the relative position of the two clusters and the orientation of each of the clusters contribute, thus both rotation and translation influence the correlation. The total intensity correlation function is than a combination of different terms

$$G_2(q, t) = G_2^{(1)}(q, t) + G_2^{(2)}(q, t) + G_2^B, \quad [2.25]$$

where

$$G_2^{(1)}(q, t) = \sum_{\alpha} \sum_{iklm} \langle \exp[iq(-\mathbf{b}_j^{\alpha}(t) + \mathbf{b}_k^{\alpha}(t) - \mathbf{b}_l^{\alpha}(0) + \mathbf{b}_m^{\alpha}(0))] \rangle, \quad [2.26]$$

and

$$G_2^{(2)}(q, t) = \sum_{\alpha, \beta(\alpha \neq \beta)} \sum_{jklm} \langle \exp[iq(\mathbf{R}_{\alpha}(t) - \mathbf{R}_{\alpha}(0) + \mathbf{R}_{\beta}(t) - \mathbf{R}_{\beta}(0))] \rangle \times \exp[iq(\mathbf{b}_j^{\alpha}(t) - \mathbf{b}_k^{\alpha}(0) + \mathbf{b}_l^{\beta}(t) - \mathbf{b}_m^{\beta}(0))] \rangle \quad [2.27]$$

The two terms, in which the first one only depends on rotation and the second one also include a translation part, are now giving us the dynamics of the correlation function. By studying the sum closer we can see that the first term scales as the number of clusters in the scattering volume, N , while the second term scales as N^2 . The number of clusters does not need to be very large before the second term is considerably larger than the first, and we can in many cases ignore the first term.

We start with the second term, and assume that the translation and rotation diffusion are uncoupled. We also assume that each cluster can be characterized by a single translation diffusion constant determined by Eq. 2.3. The last is reasonable as long as the anisotropy of the clusters is not too large. In our case with clay particles we have to be strongly aware of this assumption, since the clusters are built up by plane platelets and not spheres. It is however still possible as a first approximation that a cluster has a form not very unlike the shape of a sphere. We can now separate terms consisting of translation diffusion and rotational diffusion from different clusters, and therefore write $G_2^{(2)}$ as

$$G_2^{(2)}(q, t) = \sum_{\alpha, \beta (\alpha \neq \beta)} \exp(-\mathbf{q}(D_\alpha + D_\beta)t) I_R^\alpha(t) I_R^\beta(t), \quad [2.28]$$

where

$$I_R^\alpha(t) = \sum_{iklm} \langle \exp[i\mathbf{k}(\mathbf{b}_j^\alpha(t) - \mathbf{b}_k^\alpha(0))] \rangle \langle \exp[i\mathbf{k}(\mathbf{b}_l^\beta(t) - \mathbf{b}_m^\beta(0))] \rangle. \quad [2.29]$$

Now we have to do the averaging over the exponential functions. One way to start is by using the Rayleigh expansion [13]

$$\exp(i\mathbf{k}\mathbf{b}_j(t)) = 4\pi \sum_{l, m} i^l j_l(k\mathbf{b}_j) Y_{lm}^*(\Omega_k) Y_{lm}[\Omega_j(t)]. \quad [2.30]$$

j_l is the l th spherical Bessel function, and Y_{lm} denotes the spherical harmonics which is well known from the quantum mechanics as the eigenfunctions of the angular momentum operator $L^2 Y = m_l Y$ [11,15]. Ω_q and $\Omega_j(t)$ are the orientation of the scattering vector and the orientation of the displacement vector $\mathbf{b}_j(t)$ in the laboratory frame respectively. To make the averaging easier related to the vectors, we may transform the harmonics functions containing the displacement vector of each sub-volume of the cluster to a functions with cluster fixed orientation by use of the time dependent Wigner rotation matrix, $D_{mm'}^l$. The transformation may be written as

$$Y_{lm}(\Omega_{lab}) = \sum_{m'} D_{m'm}^l(\Omega_T) Y_{lm'}(\Omega_{cl}), \quad [2.31]$$

where $\Omega_T = (\alpha, \beta, \gamma)$ is the Euler angles transformation between the cluster fixed and laboratory fixed frame. Now the only time dependence is apparent in the Wigner matrices and the transformation Euler angles, Ω_T , since the sub-volumes of the cluster now have a fixed orientation in the cluster. The time averaging is then isolated to be calculated from the joint probability for the cluster fixed coordinate system to have a orientation angle $\Omega(t)$ at time t and $\Omega(0)$ at time $t=0$. We now assume that the overall anisotropy of the clusters is small, and the clusters may then be considered as spheres with a hydrodynamic radius of R_H^α . The rotational coefficient for a spherical particle is then represented as $\Theta_\alpha = k_B T / 6\pi\eta(R_H^\alpha)^3$. Whence the joint probability for the orientation for a cluster is [10]

$$G(\Omega(t), t | \Omega(0), 0) = \frac{1}{8\pi^2} \sum_{J, K, M''} \frac{2J+1}{8\pi^2} D_{KM''}^J(\Omega_T(0)) D_{KM''}^J(\Omega_T(t)) \quad [2.32]$$

$$\times \exp(-l(l+1)\Theta t)$$

Now we have to integrate over all incident room angles and all room angles at time t multiplied by the joint probability in Eq. 2.32 and we obtain the time averaging [13]

$$\langle D_{Mm}^l(\Omega_T(t)) D_{M'm'}^{l'}{}^*(\Omega_T(0)) \rangle \quad [2.33]$$

$$= \frac{1}{8\pi^2} \sum_{J, K, M''} \frac{2J+1}{8\pi^2} \exp(-l(l+1)\Theta t)$$

$$\times \int d\Omega_T(0) \int d\Omega_T(t) D_{KM''}^J(\Omega_T(0)) D_{M'm'}^{l'}{}^*(\Omega_T(t)) D_{Mm}^l(\Omega_T(0)) D_{KM''}^J{}^*(\Omega_T(t))$$

$$= \frac{1}{2l+1} \delta_{ll'} \delta_{MM'} \delta_{mm'} \exp(-l(l+1)\Theta t)$$

We now use the relation

$$\sum_m |Y_{lm}(\Omega_q)|^2 = \frac{2l+1}{4\pi}, \quad [2.34]$$

which together with Eq. 2.29 - Eq. 2.33 gives the second term of the correlation function

$$G_2^{(2)}(q, t) = \sum_{\alpha, \beta (\alpha \neq \beta)} \sum_{l, l'} S_l^\alpha(q) S_{l'}^\beta(q) \exp(-q(D_\alpha + D_\beta)t) \quad [2.35]$$

$$\times \exp(-[l(l+1)\Theta_\alpha + l'(l'+1)\Theta_\beta]t)m$$

where the S_l^α terms is a multipole expansion of cluster α and represent the internal structure of the cluster and is given as

$$S_l^\alpha(q) = \sum_m \left| \sum_i j_l(\mathbf{q}\mathbf{b}_i^\alpha) Y_{lm}(\Omega_i^\alpha) \right|^2, \quad [2.36]$$

To calculate $G_2^{(1)}$ we only have to look at Eq. 2.35. $G_2^{(1)}$ is as previous described independent of translation and the difference is therefore that the first summation is only over one index, α , and the exponential containing the translation diffusion constant will vanish

$$G_2^{(1)}(q, t) = \sum_{\alpha} \sum_{l, l'} S_l^\alpha(q) S_{l'}^\alpha(q) \exp[-l(l+1) + l'(l'+1)] \Theta_\alpha t. \quad [2.37]$$

As mentioned the $G_2^{(1)}$ scales as N and for the experiments presented in this report, the scattering volume is large enough to ignore this term and just take into account $G_2^{(2)}$ which scales as N^2 .

2.2.6 The structure factor and multipole expansion

It is not in the range of this report to go into details about how the multipole expansion terms, $S_l(k)$, of the clay suspension behaves. It is obvious that a closer theory for how the expansion for sodium fluorohectorite need more specific knowledge about the structure of the clay and how the cluster aggregates of clay platelets are created. It is however interesting to have a look at expansions done by previous experiments and simulations of simpler and well known systems.

For some fractal structures of spherical particles the DLS seems to show some universal behaviour. By carefully using scaling techniques it is possible to scale the experimentally found diffusion constant, represented by the first cumulant («Polydispersity and rotation. Cumulants.» on page 15), on to a universal master curve dependent of the qR value of the scattering [17,22]. We can see two of these master curves in Figure 2–3. This implies that a complete experimental registration of the first cumulant vs qR may give knowledge about the fractal structure of the clusters in the clay suspensions.

2.2.7 The effect of the scattering volume

Under more realistic conditions than presented in the previous sections, the normalized auto-correlation function must be adjusted by a pre-factor of the exponential term as follow

$$G(\tau) = 1 + f(n_{coh}) \exp(-2Dq^2\tau), \quad [2.38]$$

and corresponding if the correlation is influenced by rotation. We have $0 \leq f(n_{coh}) \leq 1$ [14], and n_{coh} represent the number of coherence areas in the scattering volume we are looking at.

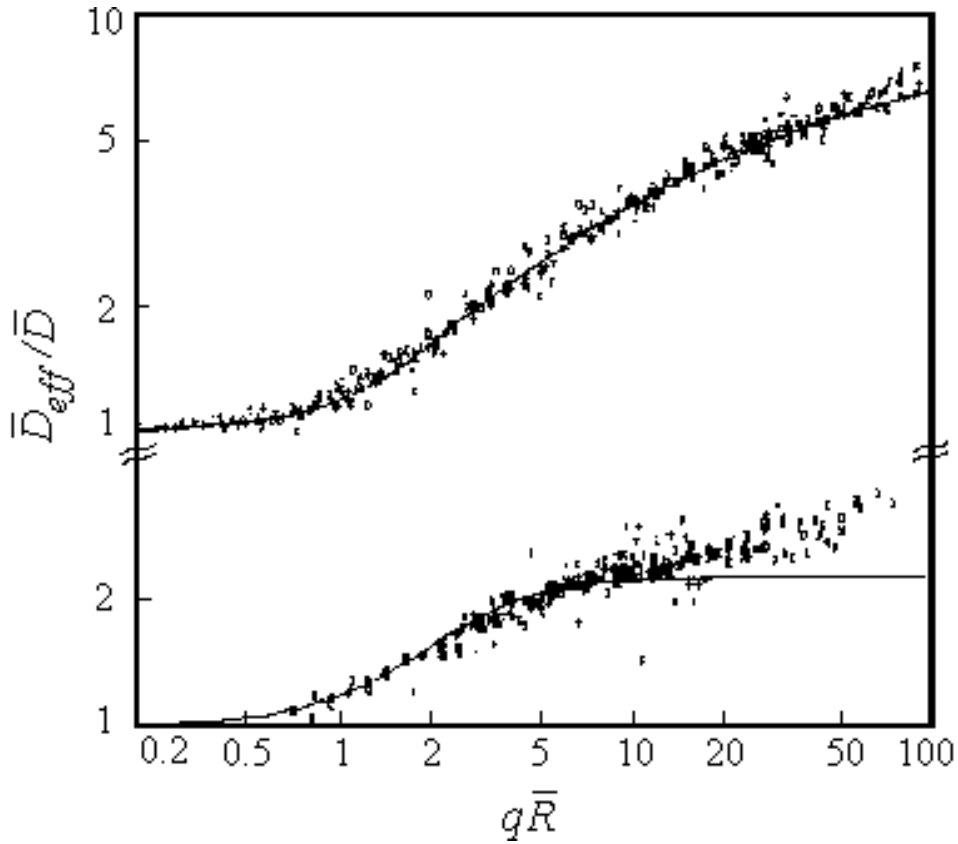


Figure 2-3: We can in this graph see a dataplot of the effective diffusion constant, D_{eff} divided by the diffusion constant if only translation diffusion was present. The effective diffusion constant is computed from the first cumulant («Polydispersity and rotation. Cumulants.» on page 15). The two graphs represent two different fractal structures, and in both graphs, although it is hard to see, there is data from gold, polystyrene and silica clusters. This states a universal behaviour when the fractal dimension of the cluster is given. We can also see that the effective diffusion coefficient is going to the translation diffusion constant when $qR \ll 1$.

To see why this is influencing the strength of the correlation we can have a look at Figure 2-4. As we can see the path length difference between the two particles is $d + d \cdot \cos(\theta)$, and the angle difference between two interference maxima at the detector (O) is

$\Delta\theta = \sin^{-1}(\lambda/d) \approx \lambda/d$ for small θ . With $\lambda=632$ nm, and a separation of particles in the scattering volume of 1mm the $\Delta\theta$ is $6.32E-4$ rad or $3.6E-2^\circ$. Thus, a detector that subtends an angle in significantly greater than $\Delta\theta$, will detect several maxima and several minima simultaneously and the averaged signal will consequently fluctuate less than for a detector with a smaller detector area. The result is a decrease in the pre-factor of the exponential, that represent the dynamic properties of the suspension. How the pre-factor, $f(A)$, is decreasing is described in Figure 2-5 [9].

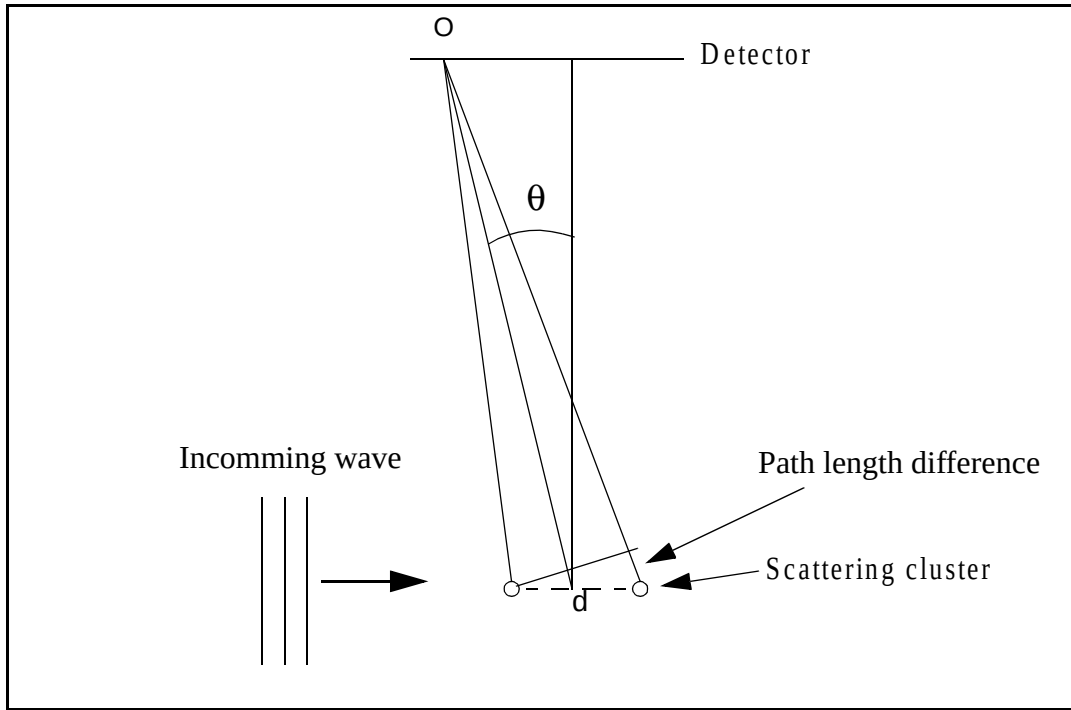


Figure 2–4: The figure show an incident wave scattered at two different clusters. We can see that the path length difference between the to scattered waves is $d + d \sin \theta$. If d is much bigger than the wavelength of the light, it is obvious that just small changes in the angle, θ , cause the intensity at O to go from a minimum to a maximum. In the case of large d , or correspondingly a big scattering volume, the light intensity in the detector thus is averaged over several maxima and is less sensitive to variations. This makes the $f(A)$ to decrease with increasing scattering volume.

2.2.8 Polydispersity and rotation. Cumulants.

We assume in the section «Brownian motions» on page 4 the particles to have the same size. To some extent it is reasonable to believe that the particles in a clay suspension show polydisperse behaviour, and they are certainly not complete monodisperse. This fact complicates the analysis a lot. The correlation function contains no longer one single decay rate, but rather an integral over the distribution of decay rates or cluster sizes, a , as follow

$$G_2(\tau) = N^2 |E_0|^4 \beta^2 \int [1 + \exp \{-(2D(a)q^2 \cdot \tau)\}] d(a) \quad [2.39]$$

If the sample now is polydisperse the analysis becomes quite complex. A perfect analysis would give the complete cluster size distribution, but the chances of obtaining these data in others than the simplest systems are virtually impossible. This has resulted in different methods which has the purpose to get at least some limited amount of data from the system. One of these methods is the use of cumulants [9] in which the correlation function is expanded as

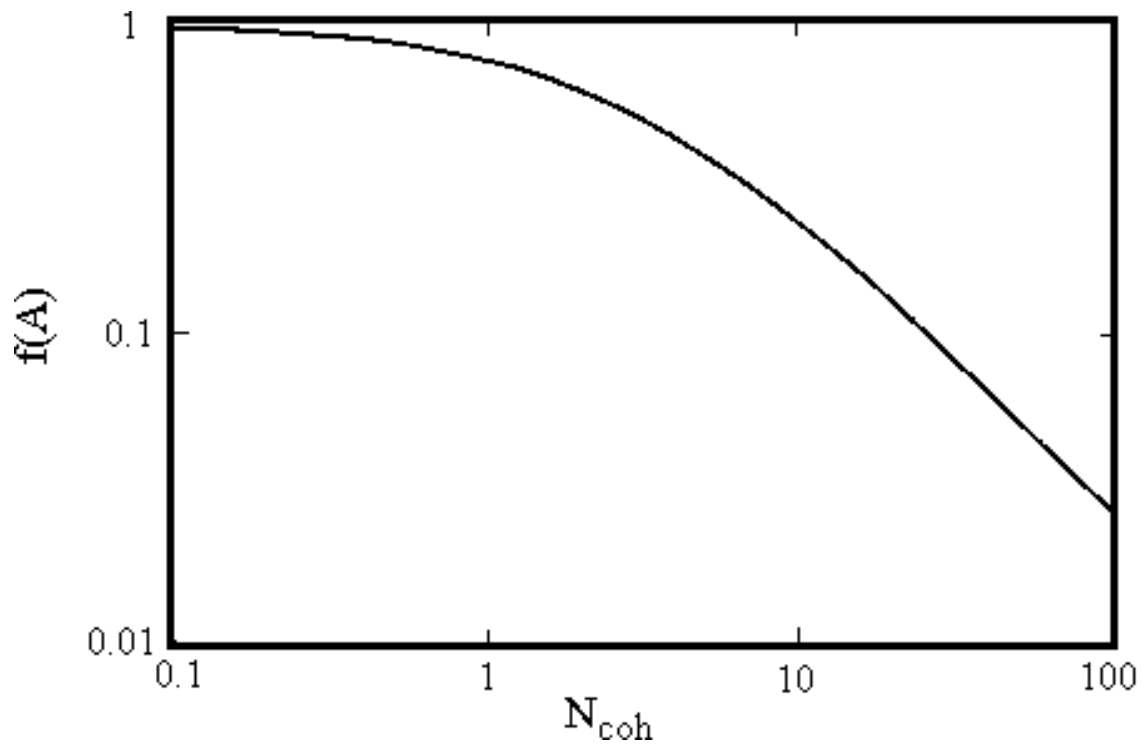


Figure 2-5: The graph shows how the pre-factor $f(A)$ of the correlation function decreases as the number of coherence areas, N_{coh} , in the scattering volume is increasing. A coherence area is defined as an area in which there exists a certain degree of coherence among all the scattering elements.

$$\frac{1}{2} \ln(G(\tau) - G(\infty)) = C_0 - K_1 \tau + \frac{1}{2!} K_2 \tau^2 - \frac{1}{3!} K_3 \tau^3 + \dots, \quad [2.40]$$

where $K_1, K_2, K_3, \dots$ are the cumulants. We can now calculate the different cumulants by differentiate the left side to the order of the cumulant we want and later let time, t , go to zero,

$$K_n = (-1)^n n! \lim_{\tau \rightarrow 0} \frac{\partial^n}{\partial \tau^n} (\ln(G(\tau) - G(\infty))). \quad [2.41]$$

The relationship between the cumulants and the properties of the distribution of the decay rates are as follow

$$K_1 = \langle \Gamma \rangle, \quad [2.42]$$

$$K_2 = \langle (\Gamma - \langle \Gamma \rangle)^2 \rangle, \quad [2.43]$$

$$K_3 = \langle (\Gamma - \langle \Gamma \rangle)^3 \rangle \quad [2.44]$$

and so on, where $\langle \Gamma \rangle$ is the mean decay rate of the system. We can see the cumulants now making us able to decide the average decay rate, the standard deviation of the distribution of the decay rates, the skewness of the distribution etc [9].

It is unfortunately so that there is not necessarily a direct relation between this decay rate distribution and the molecular size distribution, hence the conclusions should be carefully obtained due to the fact that also a contribution from rotation will lead to a sum of several decay rates as described previous in this section. From Eq. 2.35 on page 12 we see that the decay rate related to translation is coupled to the decay rate related to rotation since each of the decay rate terms is of the form

$$\exp(-q(D_\alpha + D_\beta) + l(l+1)\Theta_\alpha + l'(l'+1)\Theta_\beta)t. \quad [2.45]$$

Whence it is impossible to get accurate information of the translation dynamics through the correlation function if we do not know anything about the multipole expansion (the internal structure) or if we can not vary the scattering vector to see the $\mathbf{q}$ dependence of the correlation function. As we can see only the translation part of the decay rate has a $\mathbf{q}$ vector dependence.

A combination of both translation diffusion and rotational diffusion in a polydisperse system yield a very complex correlation function to investigate, and hence the conclusion has to be drawn with this condition in mind.

3 The experiment

3.1 Sodium fluorohectorite

3.1.1 The original sample

The clay suspension I have been investigating through the experimental work is a 2.9 w/w% sodium fluorohectorite sample with a $2\text{E}-3\text{M}$ concentration of sodium chloride, and a picture of a similar sample is shown in Figure 3–1. The clay suspension is phase separated in three

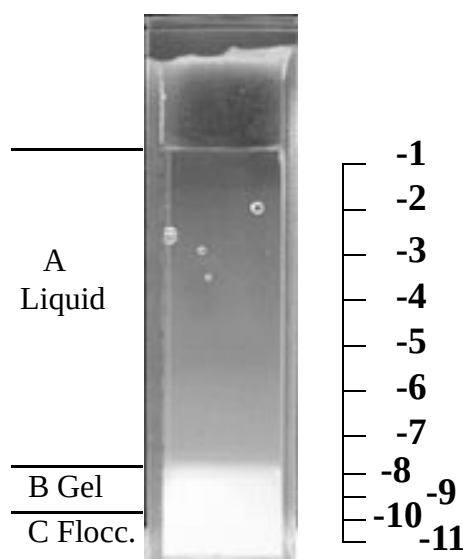


Figure 3–1: The picture shows an example of the original samples used in the experiment. The negative numbers represent the depth levels in the sample and the correlation data presented in this report refers to this classification of the sample.

distinguishable phases. The uppermost phase, between level -1 and -7, is a liquid. Level -8 and -9 represent most likely a gel phase and level -10 and -11 at the bottom is a flocculated phase. In my diploma thesis I have paid most attention to the uppermost phase in Figure 3–1 but correlation data from the other phases is also presented.

3.1.2 Preparing of sub-samples

To find the correlation function for the suspension at different depths in the sample and in addition to be sure of single light scattering, we have to take out small amounts of the suspension from every required level without disturbing the complete sample. Different solutions of doing this were discussed, but the decision fell on using a micro pipette. This pipette is constructed for taking small controlled amounts of fluids out of a suspension. The pipette was adjustable from 1 to $20\mu\text{l}$.

The complete sample was put into a hypodermic with a cut end, and left undisturbed for one week in order to stabilize. 20 μl of the sample was then taken from the suspension from the top of the hypodermic as shown in Figure 3–2. To reach the different levels of the sample, the hypodermic was adjusted and the part of the sample above the next desired level was allowed to flow over the edge of the cut hypodermic. In that way we were able to stepwise get

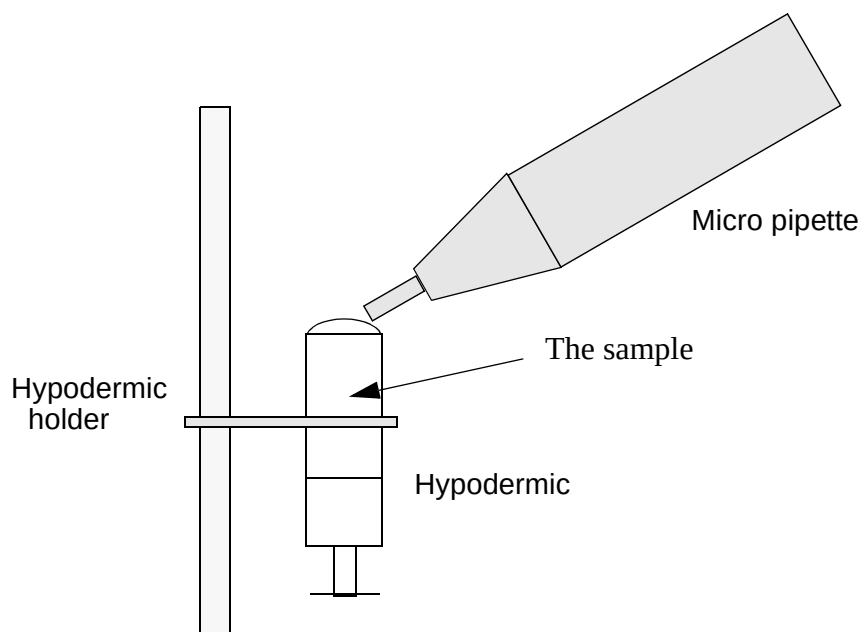


Figure 3–2: The figure is showing the hypodermic where the clay suspension was put in order to take out sub samples at different levels of the original sample. The micro pipette was used to take out 20 μl of the clay suspension at each level.

small samples for every level of the sample. The small sub-samples were put on small glasses and diluted with approx. 1ml with sodium chloride water with the same concentration of sodium chloride as the original sample.

3.2 Two correlation experiments

1. The sub-samples.

The sub-samples were prepared one afternoon and the first correlation experiment was done the morning after, approx. 20 hours later. The correlation data was collected with a total sampling time of 900 s for each of the levels. This first series is denoted in this report as *series 1*. Another 24 hours later the experiment was repeated and this data is denoted as *series 2*.

The samples were put in an optical glass vessel before the correlation experiment was done. These vessels do not polarize the light and hence do not change the polarization of the scattered light. The glass vessel was then put into a closed brass holder where the direct beam

is directed through the sample and light scattered 90° is allowed to get out of the holder through a transparent window in the holder. The brass holder was filled up with glycerol in order to stabilize the temperature of the vessel and to avoid a too high step of the refraction index when the light is entering the sample.

Before starting a new correlation run after two samples had been switched, the temperature in the metallic sample holder was allowed to stabilize at $25,00 (\pm 0.01)^\circ\text{C}$. The temperature controller is presented on page 26.

2. Scanning of complete samples

Sodium fluorohectorite samples was made with various salt concentration during my project work, autumn 1999 [7]. A complete analysis of the light scattering data from all these different samples is not a subject of my diploma thesis, the preparing and collecting work of these data is, and an example of a first analysis of a sample is presented. The samples were kept in optical glass vessels which do not polarize the light, and the correlation function for each level was achieved by using a adjustable platform which the sample was fixed to. By raising and lowering the platform different levels of the sample was hit by the laser beam without moving the optics of the experiment. Now we were able to find the correlation function through the complete sample without moving other items than the platform. The equipment used is described later on in this chapter. It is important to note that the correlation data collected do probably not show single light scattering but a rather a combination of single and multiple light scattering. This is also why the sample presented in the previous section was divided into smaller samples and dissolved in water, in order to insure single light scattering.

3.3 The experimental equipment

3.3.1 The right angle scattering

The original metallic sample holder to put the samples inside is made for 90° scattering, and a schematic overview of the experiment is shown in Figure 3–3. The beam from the laser is focused by a lens in the sample inside the sample vessel in order to minimize the scattering volume. The light scattered 90° is then focused by another lens on to the pin hole. This makes the image of the scattered beam visible in the pin hole. It is now possible to adjust the size of the pin hole on order to control the part of the scattering volume we are interested in and still have enough intensity to get a strong enough signal from the photon counting diode.

A challenge for this experiment is to line up all the components to get a photon count signal as strong as possible. Just small variations of the position of the items do influence greatly on the photon count signal from the diode, hence the order in which the different components is lined up is important. First of all the direct beam from the laser must be focused in the sample. Then we have to adjust the lens which focus the image of the scattered light on to the pin-hole. It is important that the lens is placed so far from the scattering volume that we may

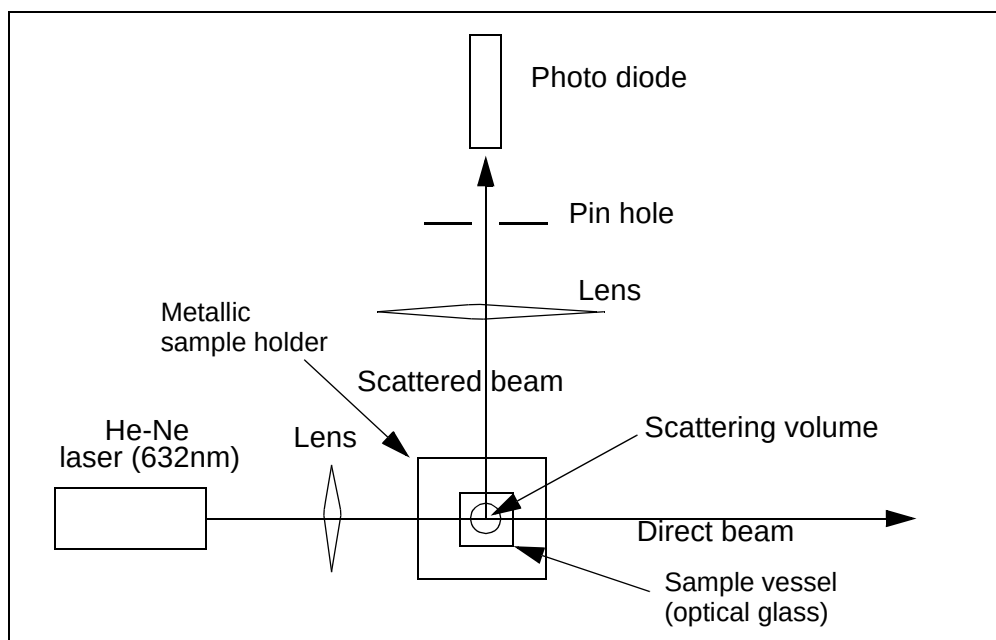


Figure 3–3: The experiment is presented in a schematic way in this figure (observed from above).

We can see that the light scattered 90° is focused through a lens onto the pin hole. An image of the beam is possible to see on the pin hole, and by adjusting the size of this hole, one can decide the size of the scattering volume we are looking at. The lens situated on the left of the sample vessel is focusing the beam in the desired volume of the sample

assume a long distance approximation (the distances which was used is shown in Figure 3–4). When the lens is fixed, it is time to adjust the pin hole in a position where the image of the direct beam is located at the pin hole. Now the photo diode has to be adjusted. To get the strongest signal possible, the signal from the diode was monitored at an oscilloscope and fixed in the position which gave the strongest signal.

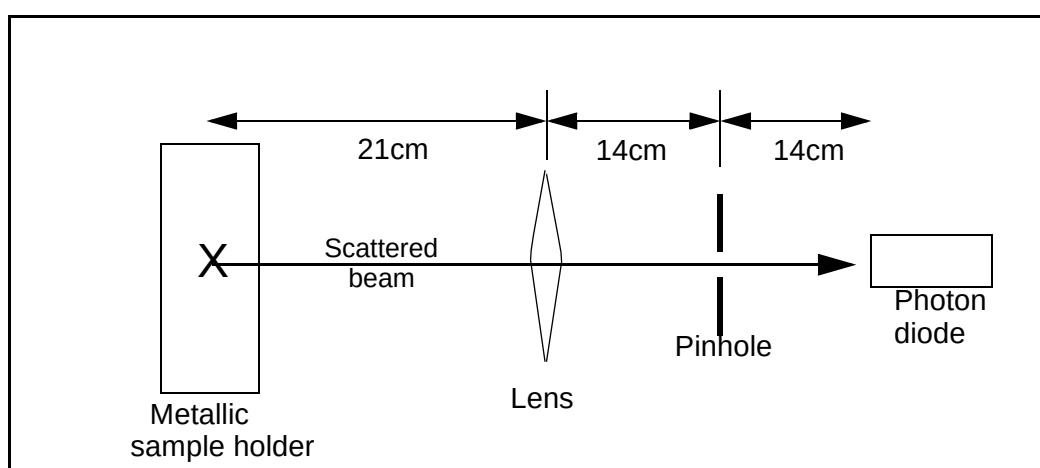


Figure 3–4: The diagram show the distances which was used in the experiment from the sample holder to the photon detector. The direct beam is entering the sample normal to the paper plane (X) and is scattered 90° .

Another effect it is important to be aware of in this experiment is light from different undesired sources apparent in the room which may influence the photon diode. This is also the case for different items reflecting the light from the laser. Especially white boards, the lenses and so on. To avoid these effects it was necessary to use black paper to screen the scattered beam as good as possible. A very sensitive part of the experiment is the distance between the pin hole and the photon diode, which was screened with a black paper tube in order to guide only the desired scattered beam on to the photon diode without disturbance. To avoid laser reflection from inside the brass sample holder, the surfaces inside the holder was painted with a black lacquer.

3.3.2 The correlator

The idea of the experiment is to find the autocorrelation function of the intensity of the scattered light from the clay suspensions and its properties (decay rates) to hopefully say something about the size of the clay clusters in the sample. As described in the theory part the size of the clusters may be found by a careful analysis of the correlation data.

The light scattered are eventually detected by a semi-conductor photovoltaic diode and the pulses are amplified, digitized and processed by the ALV-5000 Multiple Tau Digital Correlator. The correlator compute a real-time correlation function. The basic algorithm for the correlator is a step routine [19]:

1. Counting photon pulses at a sampling period, t_s
2. Delaying these samples by some integer multiple of t_s , lag time, $\tau = kt_s$
3. Multiplying delayed and direct data
4. Summing up these products

The correlator is sampling the photon pulse train from the photon diode, and the counted pulses are put in a shift register. This register takes care of all the previous counts. After one sampling time is passed, the number of pulses counted is put at the end of the register. Now the multiplying and adding procedure starts, where the recently counted number of pulses are multiplied by all the shifted data and each result is added to a separate data channel. Channel 1 is storing $n(0)n(1)$, channel 2 is storing $n(0)n(2)$, channel 3 is storing $n(0)n(3)$ and so on. Totally a number of 256 channels is taking care of the computed data. The raw correlation data is now computed as

$$G(k) = \sum_{i=1}^{N-k} n(i)n(i-k), \quad [3.1]$$

where $n(i)$ is the number of pulses detected in interval i .

It is necessary to normalize this function in some way to make different correlation functions comparable since the scattered intensity vary greatly between different experiments. To do this there is computed two temporary sums, the *direct* and *delayed* monitors represented by

$$M_{Dir} = \sum_{i=1}^M n(i) \quad [3.2]$$

$$M_{Del} = \sum_{k=1}^M n(i-k)$$

The normalized correlation output is then computed as

$$g(k) = \frac{MG(k) - M_{Dir} \cdot M_{Del}}{M_{Dir} \cdot M_{Del}} \quad [3.3]$$

To cover a wide range of lag times there is an obvious problem in combining both a very fast sampling frequency and compute the correlation function for large lag times. The ALV is operating with a sampling time of 2E-7s, which would yield a maximum lag times of approx. 60μs if the lag time was regularly separated, since only 256 separate channels are storing the correlation data. This is obviously not enough when we are interested in covering decay times up to several seconds. To avoid this problem the correlator uses a logarithmic spacing of the correlation lag time, τ (Figure 3–5 show this). Thus the correlation data for large τ are processed by averaging over several lag times in a logarithmic way. By this technique it is possible to create a correlation function which cover a much wider range of decay times than by using a fixed spacing.

Ch no.	1	2	...	8	9	...	16	17	etc
Data lag (τ)	1	2	...	8, 9	10, 11	...	16, 17, 18, 19	20, 21, 22, 23	etc

Figure 3–5: The diagram show how the data channels are storing the correlation data. We can see that the first 8 channels contain only one set of delay data. From ch. 8 to 15 however each of the channels cover two lag times. These eight channels represent therefore a double lag time compared with the eight first ones. From ch 16 we double the number of lag times covered and so on.

3.3.3 Experimental automation and programming

Some of the experiments done lasted for quite long times (the scanning of a complete sample lasted about 1 day) and demanded small adjustments frequently. The correlation data was collected at all the different levels of the sample, and between every a platform had to be adjusted to prepare for the next level. In addition a multimeter was read in order to measure the intensity of the direct beam, i.e. the light propagating straight through the sample without getting scattered. This measurement is necessary to locate the phase transitions in the sample.

To make the experiment more efficient, some automation was done. First the platform was equipped with a step motor which was run by a C program on a computer through the parallel communication port. The step motor turn one step in one direction for each time the potential on a certain pin is triggered, and simultaneously for the other direction.

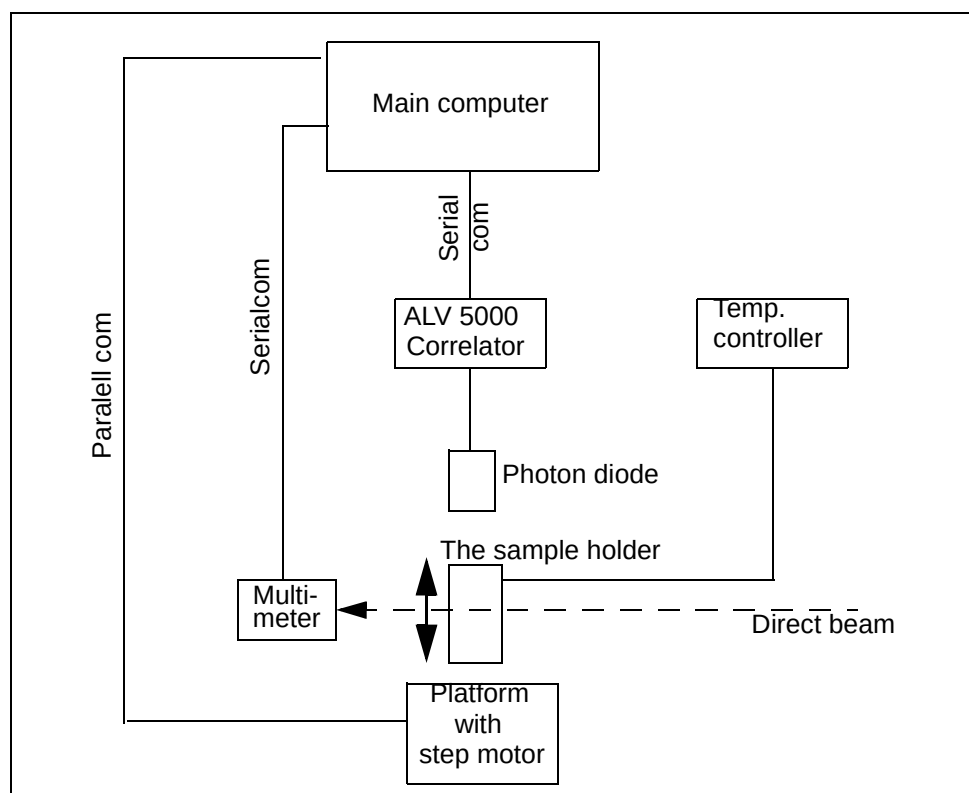


Figure 3–6: The diagram shows the computer data flow in the experiment. The main computer is controlling the ALV-5000 correlator through RS232 serial port communication, which again is sampling the pulse rate from a photo diode counting the scattered light from the sample. The ALV-5000 is installed in a separate computer. The main computer is also controlling the platform on which the sample is put. This enable a automatic scanning of a sample. The platform controlling is done through the parallel port at the main computer. In addition the intensity of the direct beam is measured by a photon diode and send to the main computer through the second serial port. Separately a computer is controlling an stabilizing the temperature of the sample vessel by adjusting a peltier element connected to the vessel, described closer on page 26.

The start of the correlation was done by starting the correlator through on of the serial ports. The ALV-5000 programme has installed a serial communication interface, and by sending characters to the port one can control the different functions in the ALV. In addition the multimeter measuring the intensity of the direct beam leaving the sample holder was read through the other serial port. All the controlling programs is written in the programming language C, and is based on some existing procedures [24] (Appendix A on page 59).

Another task which was simplified by programming was to convert the data files saved by the correlator. The ALV saved the ASCII data files in a format which was impossible for the data analysis programme, Microcal Origin, to import. I therefore had to create a programme that converted the ALV format into a format of ASCII data that was understandable for Microcal Origin (Appendix B on page 61).

3.3.4 Small angle scattering

A traditional way of doing light scattering experiments is to find the correlation function for different angles in order to see the dependence of the scattering vector. In our case as mentioned the sample holder and experimental equipment was designed in a way which made correlation for different angles very difficult. It was however worth trying, hence an attempt to collect intensity fluctuations by looking at the scattered light almost directly into the beam passing through the vessel was done. The experimental composition is shown in Figure 3–7 and we can see that intensity measurements was obtained by looking at the scattering volume through two pinholes and then tilting everything an angle θ . The lining of the pinholes and the photon diode was done by a laser which was pointing to the desired scattering volume from the position of the photon diode. This procedure is quite tedious since we had to line the components very accurate in order to avoid light from different reflections from the direct beam. The scattering angle was set to approx. 10° .

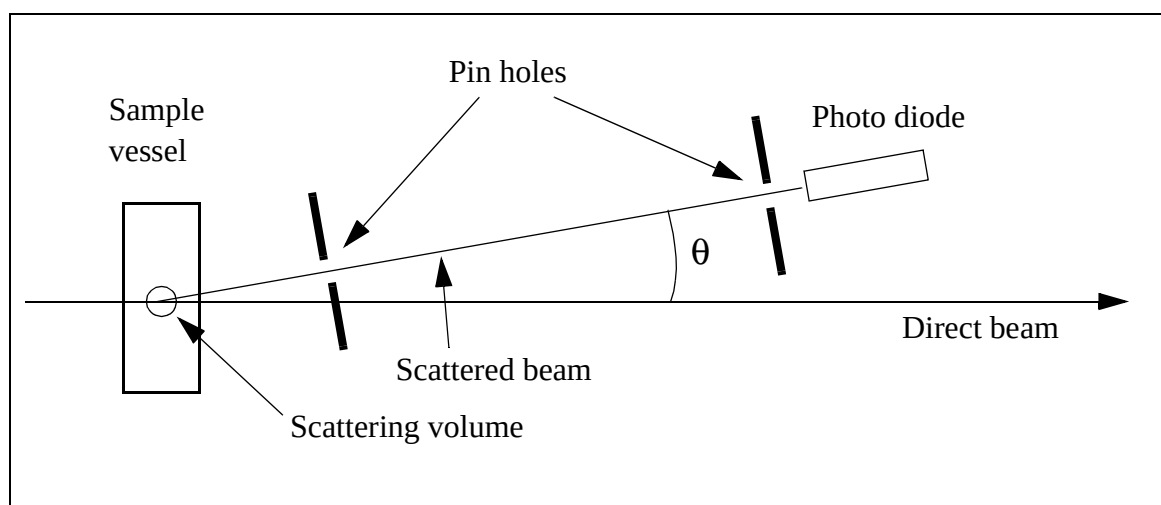


Figure 3–7: A schematic view of the small angle experiment.

3.3.5 The temperature controller

The temperature controlling system is run by a separate computer. The controlling algorithm is basically a PI regulator programmed in qBasic. The temperature is measured by a platina 100 element and the temperature is converted by a AD card before handled by the computer. A correct power signal to the peltier element is then provided by a voltage/currency converter controlled directly by the computer. The peltier element can heat as well as cool the sample. The system is able to adjust the temperature to an accuracy of 1/100 of a degree. The metallic sample vessel and the temperature regulating system is shown in Figure 3–8.

The sample holder is a system with a thermic resistance, and the different materials have of course different thermic properties. The brass sample holder is a good thermic leader while the glycol and the sample itself have a high heat capacity. This could provide temperature gradients in the system and the accurate temperature in the scattering volume is not necessar-

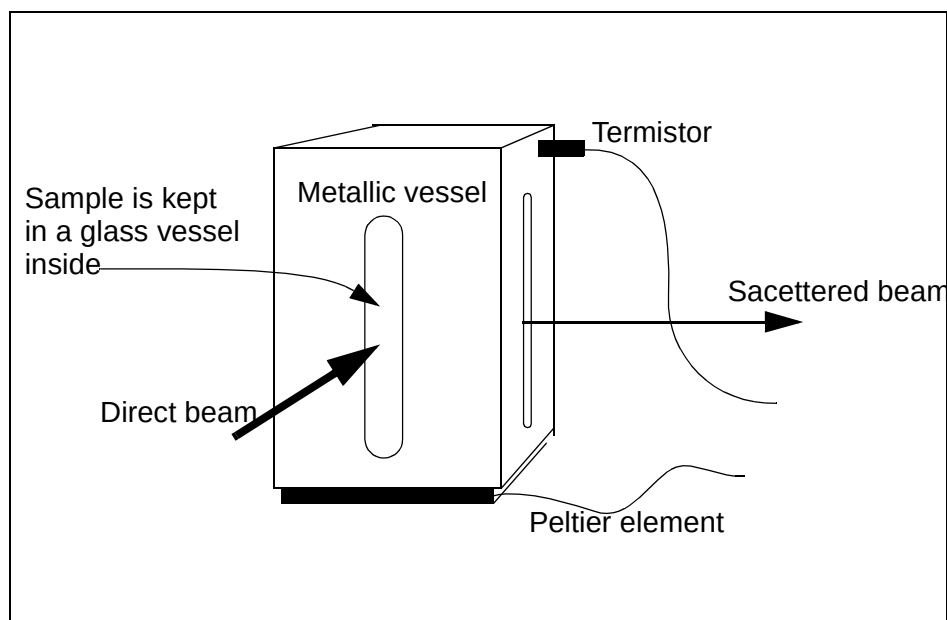


Figure 3–8: The temperature in the metallic sample holder is regulated by a peltier element and a termistor measuring the temperature. The sample is kept in a glass vessel inside the holder. We can see that the temperature measurement and the heating peltier element is separated in position, which may cause a temperature gradient inside the holder. This should however not be more than some few degrees.

ily the same as the temperature measured by the termistor at the top of the holder. Especially when the glass vessel containing the sample suddenly is put into the holder and the original temperature of the sample is deviating from the brass holder. It is additionally possible to imagine a temperature difference between the peltier heating element and the termistor even though the brass is a good thermic leader.

4 Results

This chapter will present the results of the experiments and the method of obtaining these results. The experiment is a light scattering experiment and we find the correlation function for the suspension at different levels of the clay sample. The results is hence presented as theoretical approximations and fitting functions to the collected data.

It is important to have in mind that the theory presented in the former chapters is based on an assumption that the particles or clusters are not too far from isotropic spheres. The diffusion constants for both translation and rotation are based on this since we assume hard spheres moving in a liquid solvent. The clay clusters definitely not perfect spheres, and the theory is not fitting perfectly to the correlation experiment. However by assuming a geometry not far from isotropic spheres we may although find some properties of the size distribution.

The fitting procedure was done by using the Microcal Origin fitting equipment. A closer presentation of this is seen in Appendix C on page 65.

At the end of this chapter some Atomic Force Microscope (AFM) pictures are presented. These pictures are not fully analysed, but we can visually see the contours of some clusters and get a feeling of the approx. size.

4.1 Polystyrene spheres

The correlation data was collected from polystyrene spheres of different size, first of all to learn about the experiment and the experimental technique, and secondly to see if the experiment gave reasonable data. The polystyrene spheres are provided as milky suspension with a size deviation of some percent, and they are available in different sizes. If the polystyrene spheres is left without stirring for a while, they tend to stick together in greater clusters. This will disturb the correlation function with some slower decay rates present. In order to avoid this problem the polystyrene suspensions were put in ultra sound bath for half an hour to tear up these very weak bounds between different spheres. The suspensions were then diluted by distilled water until the were almost fully transparent, to be insure single light scattering in the scattering volume.

The Figure 4–1 show a semilog plot of the correlation data for the different polystyrene spheres. A computation of the size from the correlation data, based on the theory, gives however some diverging results. All the sphere sizes are calculated to small compared with the tabulated size. Table 4–1 show the differences between the tabulated size and the computed

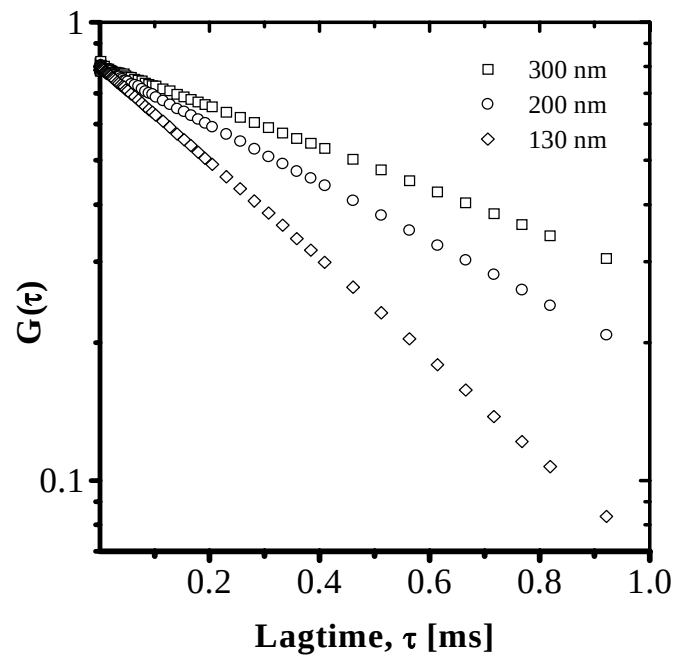


Figure 4–1: The graph shows the correlation data of the 90° scattering from different sizes of polystyrene spheres. The sizes are 130nm, 200 nm and 300 nm. We can see that the each size represent an approx. linear function in a semilog plot. This tells us that the polystyrene spheres are monodisperse particles giving a single exponential correlation function

size. The computations are first of all based on the assumption that the relation between the

Table 4–1: This table show the tabulated size of the polystyrene spheres compared with the size computed from the experimental correlation function.

Real size [nm]	Computed size[nm]	Relative factor
130	85	1.5
200	135	1.5
300	211	1.4

decay rate and hydrodynamic size is described by the Stoke-Einstein relation (Eq. 2.3 on page 5). The temperature was set to 25,00°C, the absolute viscosity of water at this temperature is tabulated to 0,890mP·s [21] and we assume a 90° scattering. The wavelength of the He-Ne laser is 632nm.

4.2 Correlation function of sodium fluorohectorite

The correlation data of the sodium fluorohectorite sample at different levels were collected and different fitting procedures were tried in order to investigate different properties of the clay suspension. The function is not as the monodisperse polystyrene spheres fitting to a single exponential function for the whole range of lag times, τ , as we can see from Figure 4–2, thus we

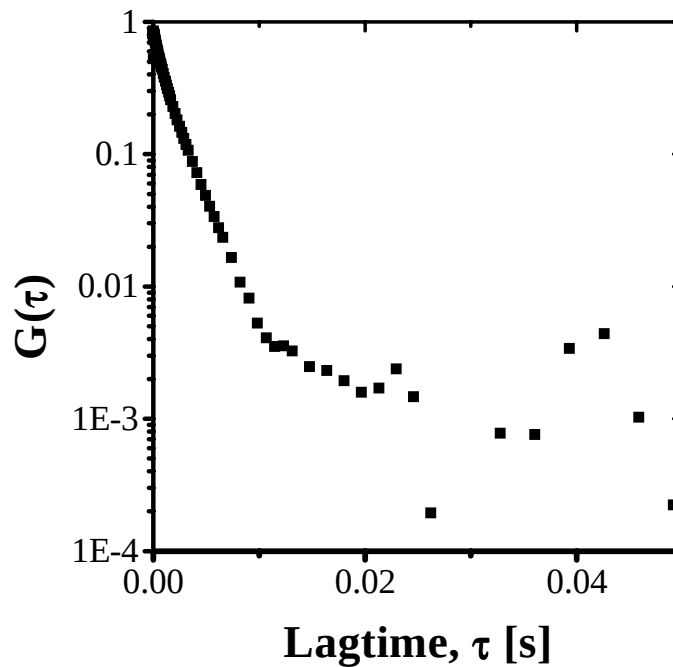


Figure 4–2: The figure show an example of a correlation data plot (the data is from the first series of the -4 depth level). The plot is steepest close to origo, and the correlation function is obviously falling off as the lag time is increasing. When we are passing $\tau=20\text{ms}$ the data seems to be influenced by some noise signal and the correlation function show casual fluctuations.

have to look at theoretical functions containing more parameters or fit the theoretical function to a shorter range of the data set.

According to the cumulant theory [10] we can decide the mean value of the decay rates of the correlation function as the lag time goes to zero, by finding the first cumulant, K_1 . With experimental data points it is difficult to evaluate a property when the data range goes to zero, but to get an estimate of the first cumulant, I assumed that the range from $\tau=0$ to $\tau=2\text{E-}4$ would at least give a good approximation.

When looking at a longer lag time range, from $\tau=0$ to $\tau=2\text{E-}2$, it is obvious that the experimental correlation data do not fit to single exponential function. A step further was to try to fit the data to a sum of two or more exponential functions or a stretched exponential function. It is necessary when fitting data to the correlation to be careful in order to keep the number of

parameters as low as possible. By increasing the number of parameters it is possible to make an apparently perfect fit but the uncertainty in each parameter will increase dramatically and the coupling between them will be stronger resulting in a fitting function which still is not reliable. Despite of this I tried to fit the correlation to a sum of three separate exponential function and a constant giving a total seven parameters. The result did exclude this model, since the amplitude factor of the third exponential decay became vanishing small, and the decay time was diverging against infinity. An exponential function with a decay time very slow compared with the others may be treated as a constant when looking at short lag times, thus fitting the correlation data to sum of more than two exponential functions was not desirable.

4.2.1 Linear fitting of the correlation function at small lag times

The simplest correlation function for translation, described in «Autocorrelation function for scattered light» on page 5, is a single exponential function. If the data is plotted in a semi log plot this results in a straight line as the polystyrene spheres is an example of. The correlation experiment of the clay suspension do not however provide a straight line and it is therefore reason to believe that the system contains more than one decay rate and most probably a distribution of decay rates. It is according to the cumulant theory interesting to have look as a first approximation at the correlation function in the first short period of lag times, τ , and try to fit these data points to a single exponential function («Polydispersity and rotation. Cumulants.» on page 15). This decay represent the fastest dynamics observed in the suspension and we may at least say something about how the properties of the clay clusters are changing when going downwards in the clay sample. The cumulant theory when we look at small lag times suggest a fit of the data to a function

$$A \exp(-\tau/\tau_1) = \exp(2C_0 - 2K_1\tau) = \exp(2C_0) \exp(-2K_1\tau). \quad [4.1]$$

This fit contains just two parameters, $A = \exp(2C_0)$ and $\tau_1 = 1/(2K_1)$, where K_1 is the first cumulant. Figure 4–3 shows an example of the fitted data to a short time range from 2E-6 to 2E-4s. The one exponential function fit quite well and the differences between the data points and the fitted data is shown in Figure 4–4. We can see that the data points close to zero is varying further from the fit than at longer lag times. The variation from the fit is however spread on both sides of the fit although it seems to be some sort of regular variation from $\tau=1E-4$ to 2E-4.

The experimental correlation procedure was repeated one day after the first correlation experiment with the same sub-samples. The fitting results of both the experiments is presented in Figure 4–5). We can see that the decay time is increasing slowly as we start to go down in the sample, but is stabilized between level -3 and -8. Going below level -8 the decay time is increasing again but now remarkably.

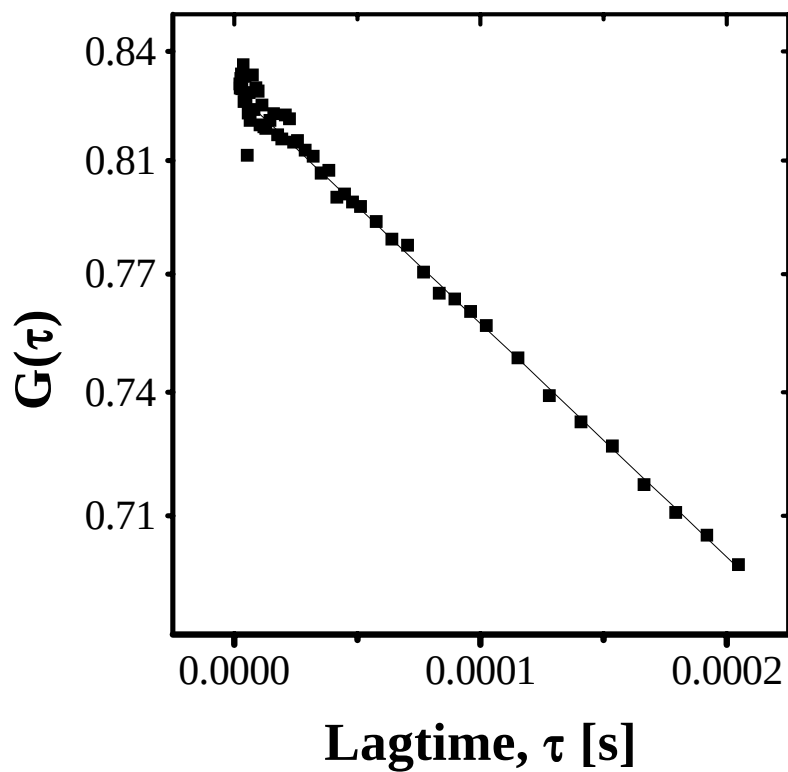


Figure 4–3: The figure shows an example of the correlation data (the black squares) for the clay sample at the level -4 and a one exponential function fit (the solid line). The plot is a semilog plot. The experimental data is fitted for lag times from 2E-6 to 2E-4s. We can see that the experimental data fit well to one decay time for this interval.

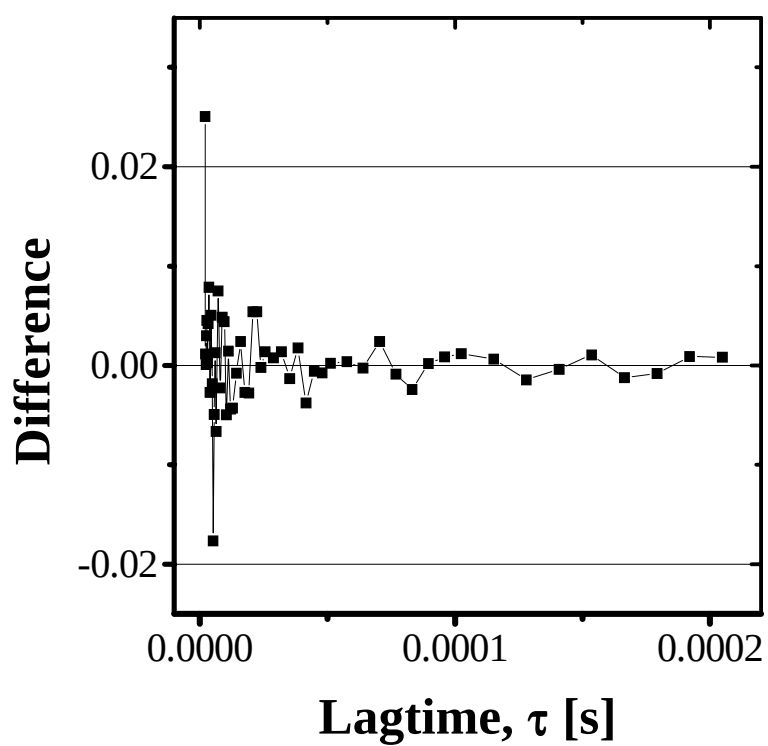


Figure 4–4: The squares show the absolute difference between the correlation data points and the one exponential function fit in Figure 4–3.

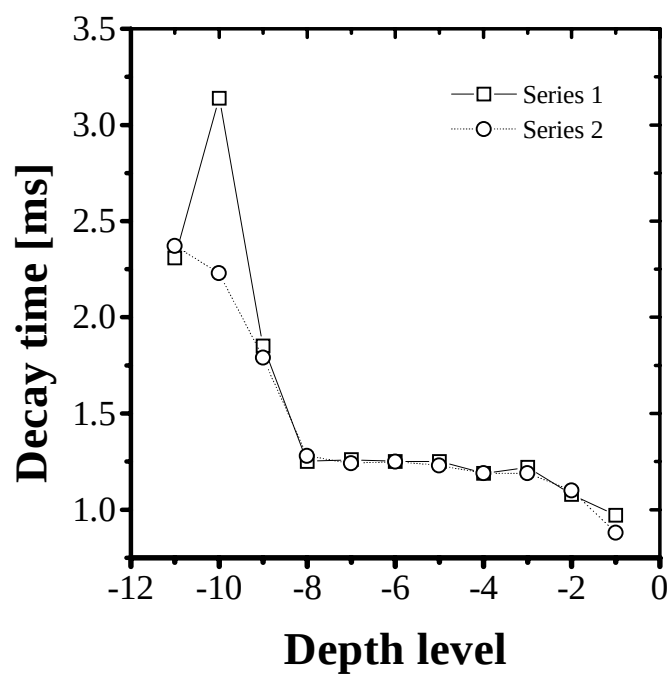


Figure 4–5: The decay time when fitting the correlation data to a one exponential function is plotted against the depth level of the sample. The fit is limited to the lag time range from $2\text{E-}6$ to $2\text{E-}4\text{s}$. The squares represent the first experimental series and the circles the second one. The two series seem to correspond at all the levels except for level -11.

4.2.2 Fitting to a sum of two exponential functions

When we are looking at a larger range of lag times, up to 0.02s, the one exponential function is not a good fit to the correlation function. Figure 4–6 show how three well defined theoretical

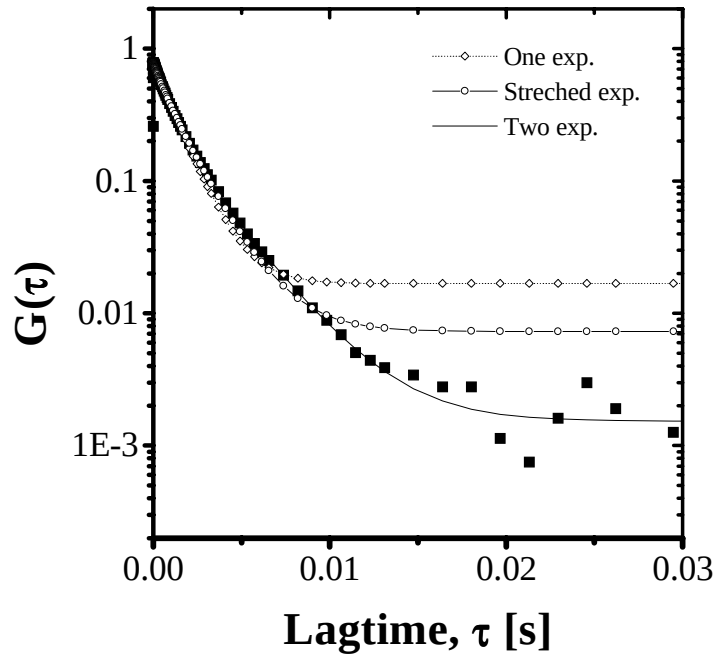


Figure 4–6: The graph shows the correlation data at the -4 level in the sample (solid squares) and different fitting functions in the range from $\tau=2\text{E-}6$ to $1\text{E-}2\text{s}$. The dotted line with diamonds is a single exponent function, the solid line with circles is a stretched exponential function and the solid one represent a fit with the sum of two exponential functions. It is obvious that the last fit seem to be the best.

functions are fitting to an example of the correlation data (the level -4 in the correlation data series 1). The first is a one exponential function plus a constant term

$$A\exp(\tau/\tau_1) + B, \quad [4.2]$$

the other is a stretched exponential and a constant term

$$A\exp(\tau/\tau_1)^\gamma + B, \quad [4.3]$$

where γ is a positive exponent, and last a sum of two exponential functions and a constant term

$$A\exp(\tau/\tau_1) + B\exp(\tau/\tau_2) + C. \quad [4.4]$$

From Table 4–2 on page 37 we can see that the chi-square value (Appendix C on page 65) is

Table 4–2: The table show how well three different function fit to the data set. The lower value of chi-square the better fit for the data plot

Model	Chi-square
One exp	9E-5
Stretched exp	2E-5
Two exp	4E-6

about one 20th for a two exponential fit compared with only one single exponent. Hence it is desirable to fit the correlation data to a sum of two exponential functions.

The fitting was done in two different ways. The first attempt was to fix the first decay rate to be equal with the decay rate found for the respective sample level when fitting the data in the short lag time range two a one exponential function described in the previous section. It is reasonable to believe that the first decay rate also would be present in the fit with a sum of two exponential functions. The second attempt was to do the fitting procedure but now allowing the first decay rate to vary as well. In order to see how the sum of two exponential functions is fitting two the data I have brought an example in Figure 4–7, showing both the absolute and relative deviation between the fit and the correlation data.

In Figure 4–8 we can see how the second decay time is developing as a function of the depth in the sample for both of the experimental series when we keep the first decay time fixed. The two series seems to differ slightly from each other.

Now we try to use the same model (Eq. 4.4) but let the first decay time vary in the fitting procedure as well. Figure 4–9 shows a plot of the two decay rates for both of the experimental series.

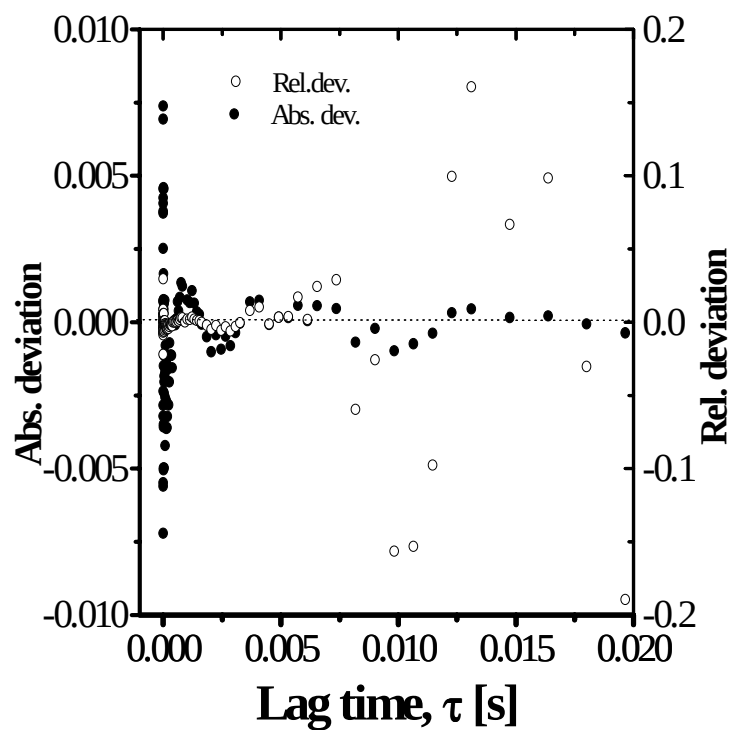


Figure 4–7: The plot represent both the relative and absolute deviation between the correlation data and a fit with two exponential functions and a constant at the depth -4 from the first correlation series. We see that the deviation is distributed on both sides of the zero line, although there seems to be some regularity in the deviation. We also note that the relative deviation is increasing remarkably when passing $\tau=0.01$ s.

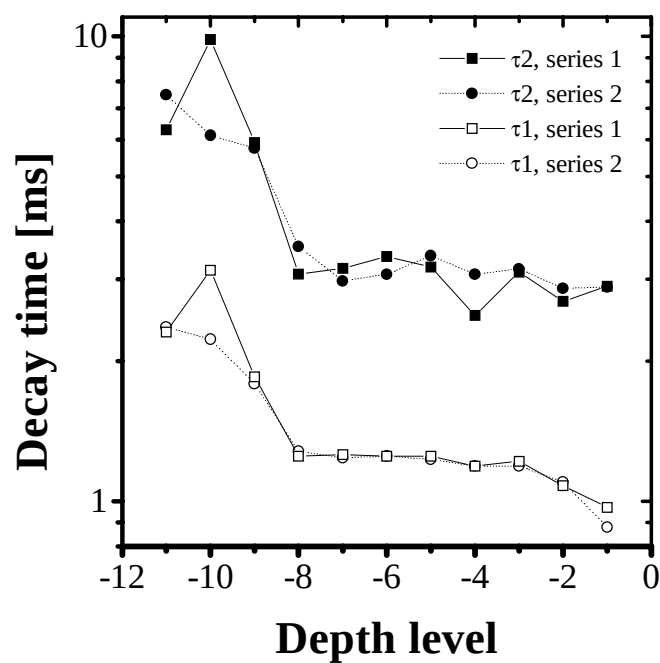


Figure 4–8: The figure show a semilog plot of the decay times for a two exponential function fit to the correlation data plotted against the depth level in the sample. In this fit the first decay time is kept fixed and equal to the one exponential fit presented in Figure 4–5 on page 35. Both the experimental series are included in this plot.

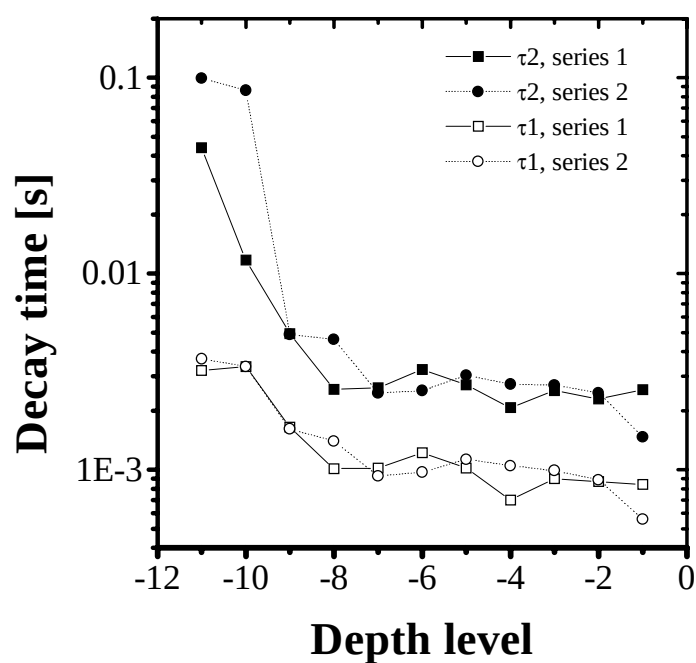


Figure 4–9: The graph show the two decay times plotted against the depth level in the sample when both of them are allowed to vary during the fitting procedure. Both of the experimental series are included in the plot.

4.2.3 The scanning of the sample

Although complete analysis of the correlation data collected when scanning the different clay samples is not integrated in this diploma thesis it is interesting to have a look at some of the first properties withdrawn. The experiment was carried out in an automatic way with the actual sample fixed to a platform driven by a step motor. For every millimetre in the sample the correlation function for the respective level was found. The total correlation time for each level was set to 300s.

The data is fitted as a first approximation to a single exponential function in the lag time range from $\tau=0$ to $\tau=1$ ms and the results are shown in Figure 4–10. For the uppermost

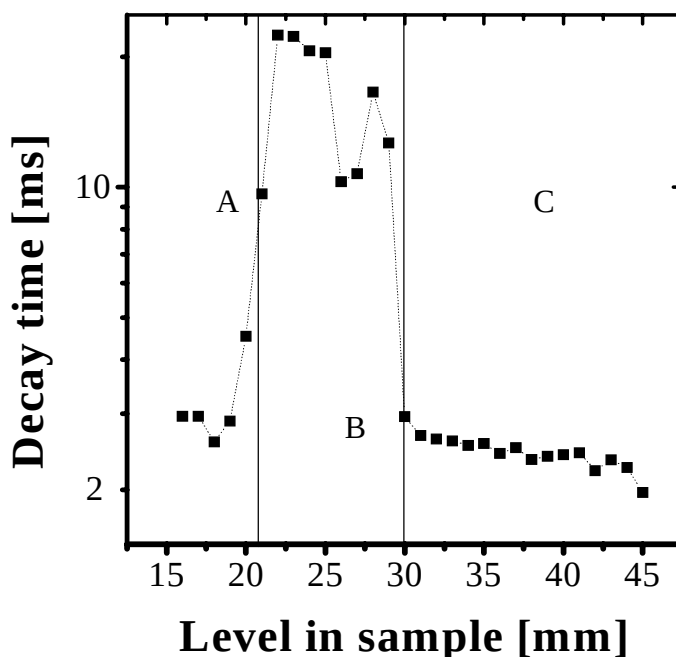


Figure 4–10: The plot show the decay times for a one exponential function fit of the correlation data when finding the data by scanning through a sample. This sample has the same properties as the sub-samples presented in this report. The fitting lag time range is from $\tau=0$ to $\tau=1$ ms. Region C is the uppermost and liquid phase of the sample. The vertical lines represent the visual observed phase transition lines. There is remarkable steps in the fit when passing these lines. It is however only region C in which the scattering process is probably governed by a single light scattering regime. In both region A and B the photons are probably scattered several times and hence we have multiple light scattering.

region, the liquid region (C), there is a corresponding result between these decay rates and the second decay times for the correlation function in the small sub-samples of, with decay times $\tau_2 \approx 2.5$ ms. As we also may observe, the decay times are changing considerably at the vertical lines in the graph. These lines represent the visually observed phase transition lines in the

sample. A great deal of uncertainty is however apparent related to the analysis of the correlation data, especially since we do not know exactly the concentration of particles in the suspension. Region C is probably governed by a simple light scattering regime, i.e. the particle concentration is below a limit where photons are statistically scattered at most ones during their way through the scattering volume. In this region it is possible to use the decay rates directly as an indication of the diffusive motions in the suspension whether it is caused by translation or rotation. In region B a higher concentration of particles makes it impossible to do the same assumption, and the light scattering process is most likely a combination of single light scattering and multiple light scattering. The concentration seems even higher in region A since it is a flocculated phase and we may assume a complete multiple light scattering regime.

4.2.4 A distribution of the cluster sizes

The system of clay clusters is obviously not ruled by only one decay rate as the one exponential fits show. A more natural situation is at least a sum of several decay rates or more likely an integral over a distribution of rates. The shape of this distribution is not known at all, since we initially do not know the particle size distribution (which is a task for this diploma thesis to say something about), and secondly the structure of the particles is not well defined, whence we cannot say how the rotation diffusion contributes to the decay rate distribution.

A first approach to this problem is to assume a well known distribution with a set of parameters and then fit this to the data set. A gauss distribution was chosen in order to at least see if it was to some extent fitable to the experimental data. The result is shown in Figure 4–11, and as we can see the distributional function is close to the sum of two exponential function fit, although the parameters of the distribution is chosen by just trying and failing for some times. The distribution in the Figure 4–11 has a mean decay time of 1,5 ms and a variance of 0,6 ms. A computational fitting procedure for all the data would give more accurate properties of the distribution. The fitting procedure will because of the distribution contain an integral for each lag time value at each fitting step. This demands a lot data power and a better understanding of numerical integration since the computation has to be numerically. The MatLab programme used is presented in Appendix D on page 67.

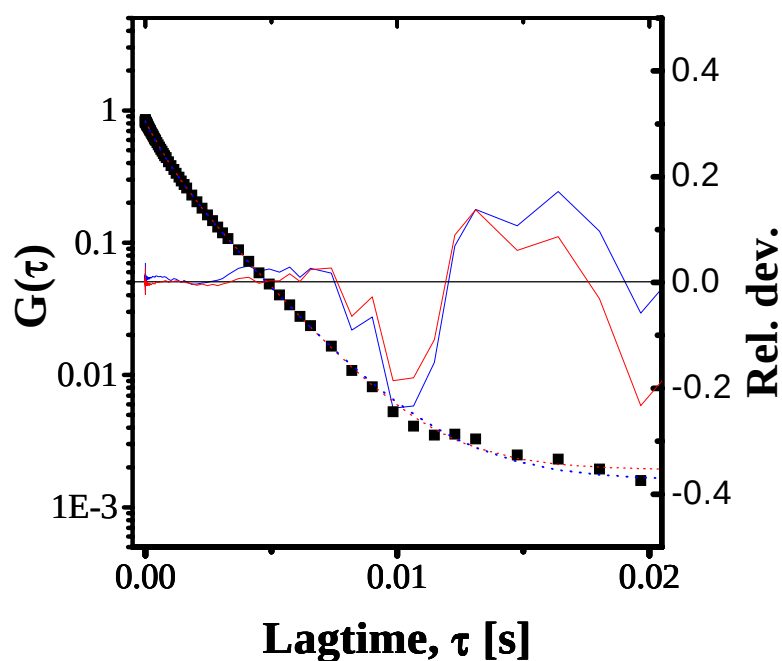


Figure 4–11: The solid black squares show the data for the correlation function at the depth level -4. The blue dotted line represents a theoretical correlation function when the decay rate distribution in the suspension is assumed to be a gauss distribution. The mean decay rate is 1,5 ms and a variance of 0,6 ms. The red dotted line is the best fit for the data using a two exponential function fit. The blue solid line is the relative deviation between the correlation data and the distribution fit and the red solid line is deviation from the two exponential function fit.

4.3 The small angle scattering experiment

A detection of the light scattered in small enough angles will according to the theory make us able to isolate the effect of the translation and neglect the rotational contribution. To get the variable kR_g small enough we have to go to angles maybe as low as 1° . As a first approach small angle scattering at approx. 10° was tried. An example of the result of the scattering is presented in Figure 4–12 and we can see that the data is influenced strongly by some oscilla-

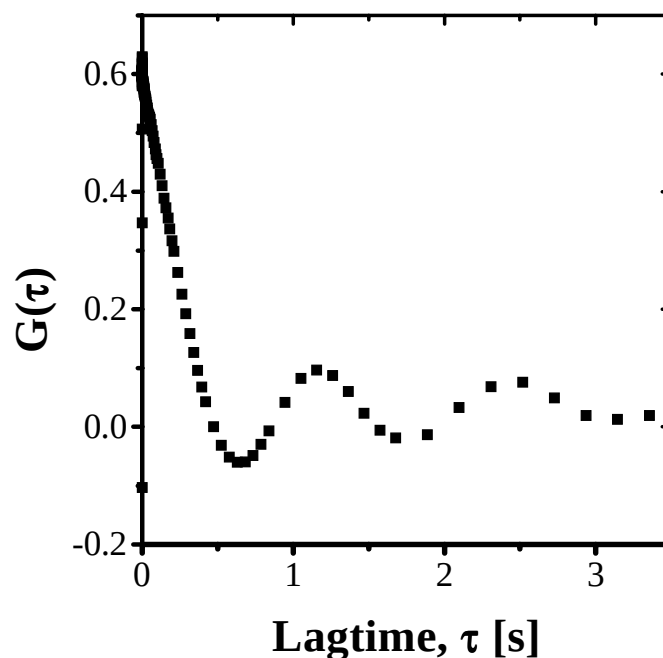


Figure 4–12: The graph show the correlation data for a small angle scattering experiment (approx. 10°). We can see an oscillations in the correlation data, which seems to have a period of approx. 1s.

tions with a period of about 1s. It is not obvious where these oscillations are originated from, but three possibilities are most likely:

1. Vibrations in the pin holes
2. Fluctuations in the laser intensity
3. Reflections inside the sample holder giving beating phenomenon

Dued to the lack of time it was not possible to investigate the cause of these oscillations more. It is however reason to believe that the laser is quite stable since there were no signs of oscillations in the 90° scattering.

In addition there has been observed beating phenomenon in similar light scattering experiments [23], and the reflex was successfully removed by a careful use of mirrors. It is possible

that back scattering reflection because of the transparent windows of the sample holder create beating phenomenon in small angle scattering, but this remains to prove.

4.4 AFM pictures

At some earlier stage there has been taken some AFM microscope pictures of the same clay suspension [16]. The pictures is not thoroughly investigated, but some basic visual analysis may at least give some first approximations of the clay cluster size. In Figure 4–13 to Figure 4–15 we can see the AFM pictures for a 50 μm , 10 μm and a 1 μm scaled plot respectively. All the pictures are from the uppermost phase (the liquid phase) from the clay suspension. The 50 μm scaled picture (Figure 4–13) is presented just to give an overview of the dried clay. On the 10 μm picture (Figure 4–14) it is possible to see particles (yellow areas) which may indicate the size of the clusters. The clusters are indeed not monodisperse and the size as we see them is varying between approx. 100nm up to 1 μm . If we study the 1 μm scaled picture (Figure 4–15) we can see some areas which most likely represent different clusters. From this detailed picture we can see areas which probably is separate clusters with size about 200nm and bigger.

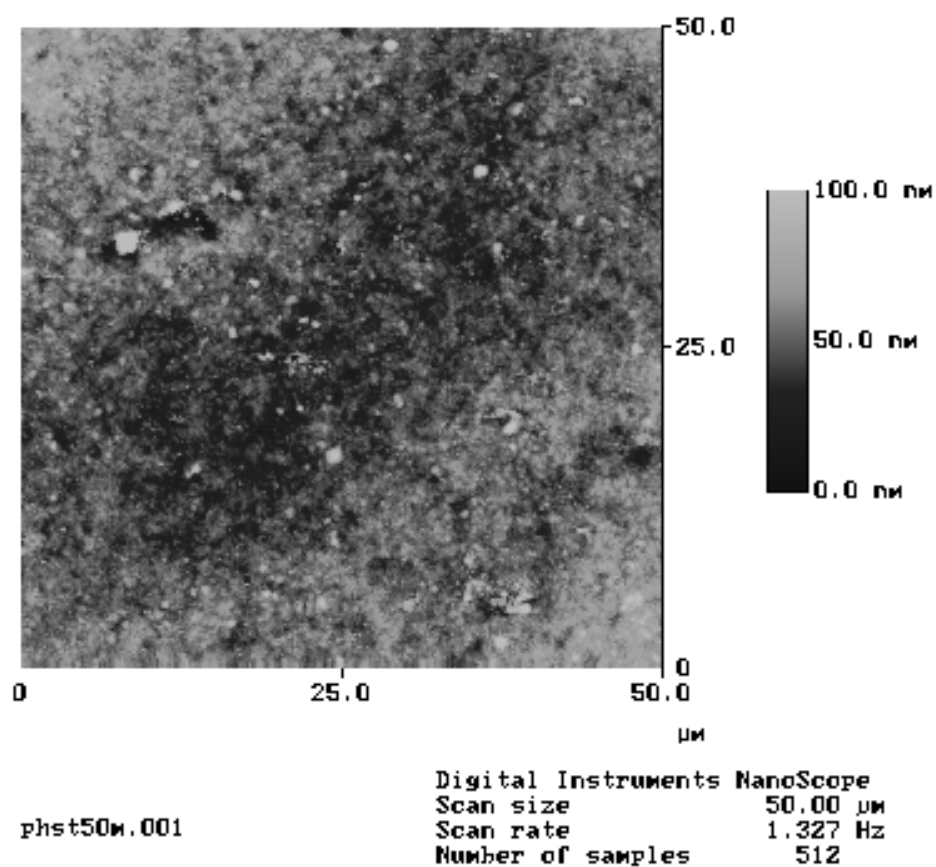


Figure 4–13: The picture is a AFM scanning of a dried clay suspension similar to the suspension presented previously in this report. The size of the particles is not possible to distinguish except some few big particles (white areas) spread around. These areas is of a diameter of several μm

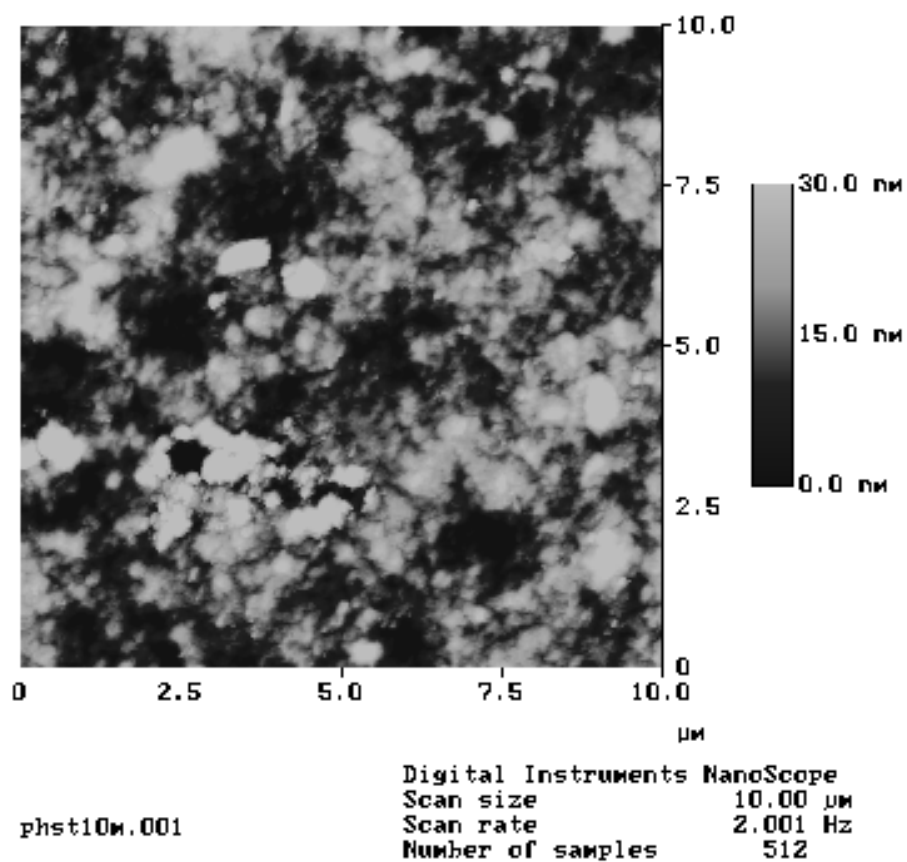


Figure 4–14: The figure show a scan with a scale of $10\mu\text{m}$. We can see particles (white areas) of different sizes, from some hundred nm to $1\mu\text{m}$.

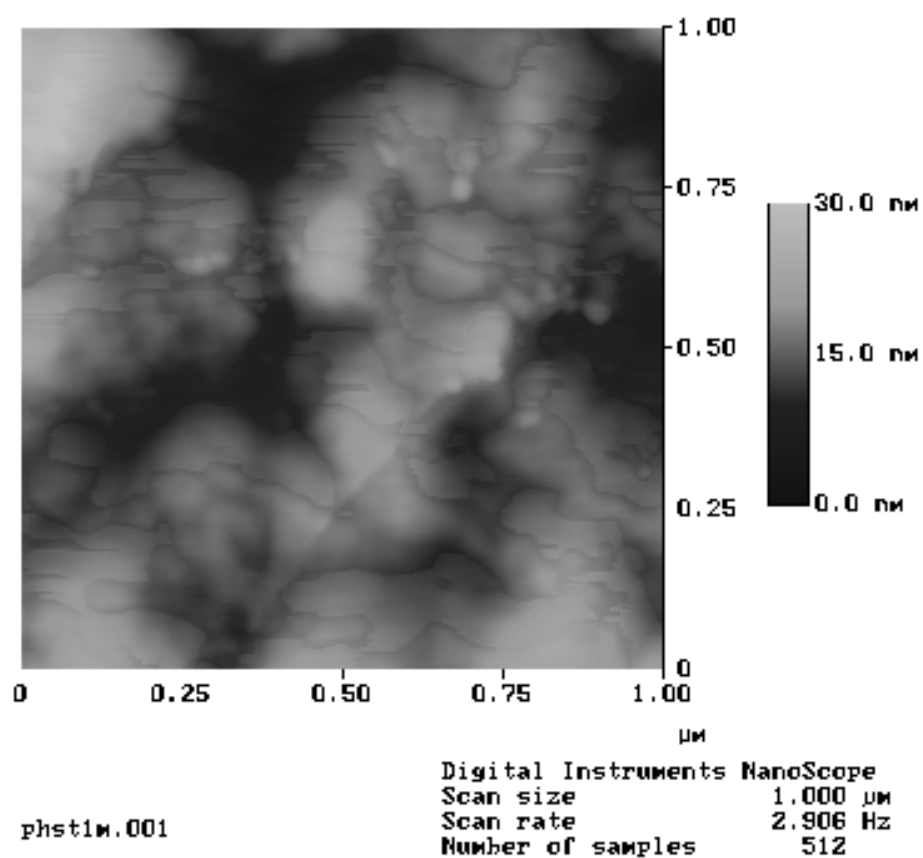


Figure 4–15: From this AFM picture which has a length scale of $1\mu\text{m}$ we can see the contours (black solid lines) of possible clay clusters of about 100nm and upwards.

5 Discussion

5.1 Polystyrene spheres

The data for the polystyrene spheres represented in Table 4–1 on page 30, show a deviation between the size computed from the correlation data and the tabulated values from the producer of the particles. All the three sizes seem however to have the same quotient between the tabulated and the calculated size, $Q = (\text{tabulated})/(\text{computed}) \approx 1.5$. Since these deviations are equal for different spheres and for different experiments, we have to look for reasons in the computations. From the Stoke-Einstein equation (Eq. 2.3 on page 5) and the theoretical function for the correlation for Brownian particles (Eq. 2.19 on page 8) the decay rate is

$$\frac{1}{\tau_1} = Dq^2 = (k_B T / 6\pi\eta a) q^2. \quad [5.1]$$

In this eq. both the temperature, the viscosity and the scattering vector are uncertain quantities.

First of all the temperature in the scattering volume may have been different from the temperature in the thermistor measuring the sample temperature. The temperature is measured at the top of the metallic sample holder and the polystyrene spheres are in a glass vessel near the bottom of the metallic vessel. The peltier element is attached to the bottom of the metallic vessel, and hence the temperature may be higher near the bottom than at the top of the metallic vessel. Let us assume there is a temperature difference of maximum 2°C. The temperature is also influencing the viscosity since $\eta = \eta(T)$, dependent on temperature. If the temperature is 27°C instead of 25°C as the thermistor in the temperature controller is showing, the computed size of the spheres will increase with 5%.

The length of the scattering vector may also contribute to a wrong computed size. If the true angle in which the detected light is scattered is different from the one assumed, this will cause a wrong answer. A rough estimate if we assume the scattering angle to be 100° instead of 90°, gives us a computed size which is approx. 20% higher. Totally this influence will decrease the quotient between the tabulated and computed size to be approx. 1.2. This leaves us still with a difference which is unfortunately not within the limits of this work to explain.

5.2 Average cluster size limit

A main challenge in this diploma thesis is to say something about the mean size of the clusters in the clay suspension of sodium fluorohectorite, which did not turn out to be trivial. First of all the light scattering technique is a complex method of science, and secondly the structure

of the clay in this suspension is not classified by former work making it difficult to separate between translation and rotational contribution.

It is however some information from the experiments presented that may at least give some ideas about limits of the cluster size. A lower limit for the size is possible to give from the fastest decay rate measured. From the theory we can see that when $kR_g \ll 1$ the rotational diffusion is not contributing, since the scattering vector in this case is too small to resolve the internal structures of the cluster. If the cluster size is within a range where this condition is valid, we can conclude that the decay time represent the translation diffusion and hence is directly proportional to the size of the clusters. Suppose now that this condition is not valid, and the rotation do contribute to the correlation function. The fastest decay rate measured is now in addition related to the rotation of the clusters. It will however still work as a lower limit for the mean cluster size. To see this let us study the term

$$S_l(k) \exp[(-2Dq - 2\Theta l(l+1))\tau] \quad [5.2]$$

which the correlation function is built up with. The size distribution is represented by a set of diffusion constants, D , but since the rotational diffusion contributes there exists terms as Eq. 5.2 where l is different from zero. This will give total decay times for the system which are faster than if only translation (only the diffusion constant D) was present. Hence decay times caused solely by translation motion in a polydisperse system will for sure be slower than if we include rotational diffusion in the system. Thus the first cumulant representing the mean decay rate in the system is a lower limit for the cluster mean size. In Figure 5–1 we can see the limiting size of the clusters when we assume the fastest decay rate limiting the cluster size. From this we see that the mean size of the clay clusters from level -3 to -8 is approx. 120nm. We also see that this limit is even smaller in level -1 and -2.

From the fitting of the correlation function it is important to have in mind that it was impossible to detect decay rates faster than approx. 1E-5s, which directly transformed into a cluster size by the Stoke-Einstein relation will give a radius of approx. 10nm. We are not able to use the correlation data for this first interval due to the fluctuations in the correlation data in the lag time range from 2E-7 to 1E-5s (the fluctuations are for instance seen in Figure 4–4 on page 34).

Another indication of the size limit, is the AFM pictures. From the pictures a normal size of the clusters is 200nm and higher. Some few clusters is observable smaller than 200nm but the mean size seems to be, by visual observations, bigger than 200nm.

5.3 The fitting functions

The correlation data for the different levels of the origin sample seem to fit well to a sum of two exponential function when looking at the lag time range from 2E-7 to 2E-2 s of the experimental data. For longer lag times the data behaves rather unsystematic and it is impossible to fit the data well to one or a set of theoretical expression. A decay rate purely related to trans-

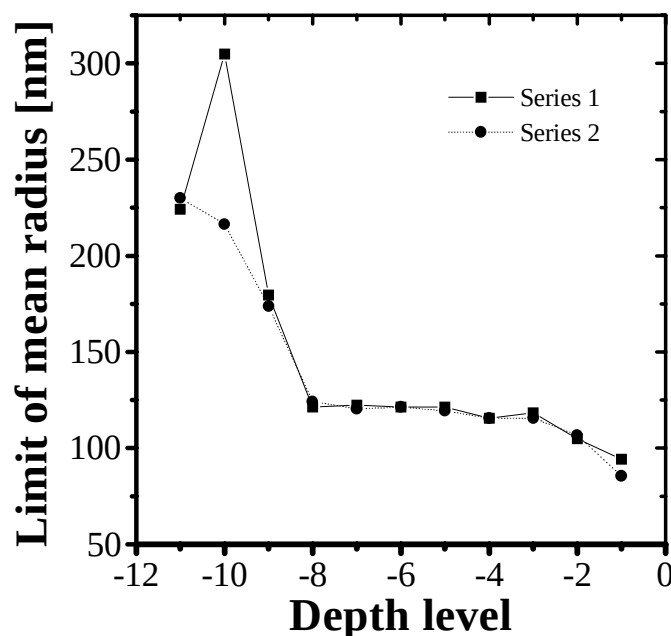


Figure 5–1: The figure shows the limited size of the clusters at each level in the sample when we assume that the fastest decay rate is limiting the mean size. Series 1 is the first measuring of the correlation and series 2 represent the second one.

lation diffusion lower than $5E-2$ would theoretically correspond to cluster sizes bigger than approx. $5\ \mu\text{m}$.

The second decay rate

Figure 4–8 on page 39 and Figure 4–9 on page 40 show the result of fitting the correlation data in two different ways to a sum of two exponential functions and a constant. In the first fit the fastest decay rate is fixed and equal to the one decay rate found in the short range fit of the correlation data. The other way was to let both of the decay rates vary.

The second decay time for both the two methods and the two experimental series is plotted in Figure 5–2. We can see that the second decay rate does not seem to change considerably while going downwards in the sample before passing level -7. This would indicate that the suspension properties is not changing through the upper phase (from level -1 to -7). At level -8 the second decay time starts to increase, and at the proceeding levels, the decay time increase strongly. For the two lowest levels, the two fitting methods show very deviating results, which probably indicates the sum of two exponential functions to be a bad model for this region. For the uppermost region however the somewhat stable second decay rate would characterize the particle size to be equal and independent of the level.

There exists however a problem in explaining this model although it seems to fit well in the actual lag time range, since it obviously does not have a probable physical interpretation.

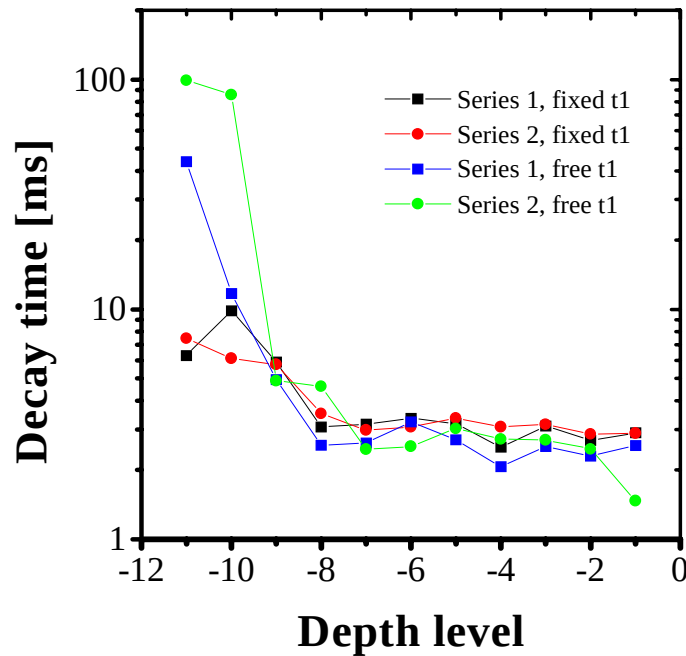


Figure 5-2: From this figure we can see the comparison between the second decay time from the two different ways of doing the fitting procedure and from the two different series of experiments. The decay times seem to harmonize for level -2 to -7, but there is deviating results for the level -8 and below.

The model require a system with two distinguishable decay rates or correspondingly two single cluster sizes or at most two narrow size distributions. It is not likely to believe that this is true for the clay. As we have seen («A distribution of the cluster sizes» on page 42) the data may as well be fitted to a simple distribution of decay rates, and the sum of two exponential function model should from that point of view just be presented as a substitute for a physical model.

The correlation data should further on be carefully analysed since some particular uncertainties is present. First of all the translation diffusion in the sample is unseparately connected to rotation. Especially is this a big problem since it was not within the limits of this diploma to get correlation data from different scattering angles, giving a q -dependence of the correlation function. From the terms of the correlation function presented in Eq. 5.2 on page 50 we can see that the translation part is dependent of the scattering vector, while the rotational part is not. Now by finding a total curve for the correlation data plotted against the scattering vector, q , we would be able to separate these two different contributions.

Another question is if the properties of the sub-samples is really the same as the properties at different levels of the origin sample. By taking out small amounts of the origin sample and then dilute them we influence this system strongly. Interruptions of the equilibrium of the system will probably start dynamic processes in the small clay samples, and the cluster distribu-

tion may then be changed. It is however a question of the speed of these dynamics, and as both the experimental series separated in time seem to harmonize we can assume the dynamical to have a weak influence.

Finally the shape of the clay particles is most important for the decay rates observed in the correlation function. As a stated condition in the theory presented in the start of this report we assume the clay cluster not to be too anisotropic, i.e. we assume the particle to be close to a sphere. As described in «The clay and clay suspensions» on page 3 the basic clay particle is a two dimensional platelet, and a likely consequence is that clay platelets aggregate in clusters not like a sphere, but with various scales in the different directions. Thus a distribution of cluster sizes do not only provide a decay rate distribution directly caused by the size distribution, but we would also probably detect different translation diffusion constant for a single cluster dependent of the orientation of the cluster As in Figure 5–3 we can assume that the

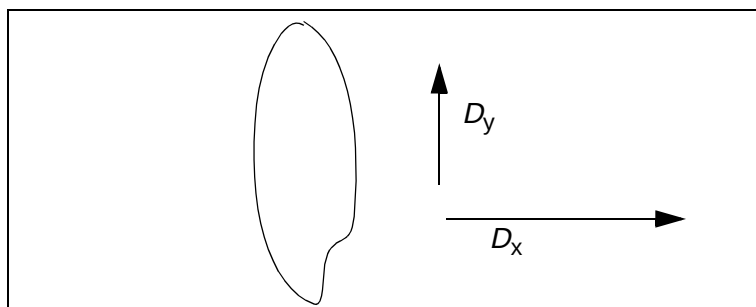


Figure 5–3: The figure show an anisotropic clay particle which we may assume have different diffusion properties dependent of the orientation.

diffusion constant in x-direction, D_x , is different from the diffusion constant in the y-direction, D_y , and by statistical averaging over the total ensemble of particles, we observe a decay rate which is some sort of combination of the specific orientational diffusion constants.

6 Conclusion

6.1 Conclusions from the experiments

The clay system studied in the previously described experiments is most probably a polydisperse system. Several observations presented in this report support this. First of all do the AFM pictures show clay clusters of strongly varying size. Even though a thorough investigation and analysis of these picture still not is done, we can see areas on the pictures which are of different size. If these ares represent clusters we may assume that the clusters size is a distributed over a range of sizes.

Another fact which support the polydispersity is the phase separating of the samples. The original sample used in this report is an example of this. A picture of a comparable sample is seen in Figure 3–1 on page 19. In a suspension of different cluster sizes it is likely that at certain system conditions particles starts to separate and different phases occurs [7].

Since we may conclude with a size distribution, a following question is what the parameters of this distribution are. This question is rather hard to answer accurately on the basis of this diploma work. The complexity of the system is very high and we have very few data of the size distribution from previous work. The cumulant theory yield, however, in the idealistic case different properties of the decay rate distribution. The mean decay rate and the variance of the distribution may for instance be found. The decay rate distribution is not unproblematicly related to the size distribution, since in the case when the cluster size does not satisfy the condition $qR_g \ll 1$, the internal structure of each cluster starts to contribute, and rotational diffusion in the system will affect the correlation function. The first cumulant give still the mean decay rate in the system, and rotational diffusion contribution implies a faster decaying correlation function than if only translation diffusion was present. Thus we may conclude that the mean size of the clusters is limited downwards by the first cumulant. From Figure 5–1 on page 51 we can see the computed limit for the mean size to be 120nm for the levels -3 to -7. For level -1 and -2 the cumulant give even a faster decay rate and hence a smaller limit size. We can explain this occurrence in the top of the sample as a sort of phase separation, and it is possible that a fourth phase is being created at the top of the sample. In this region the clay clusters is even smaller than in the liquid region below, and perhaps the particles is just single clay platelets. For the levels below -7 the decay time is increasing remarkably which should indicate that the size of the clusters is increasing. This is likely to believe since we are entering a new phase as we may observe visually. It is however impossible to give any more accurate conclusions of the size in this region.

The sum of two exponential functions seem to fit the correlation data in the uppermost liquid phase rather well, since the decay rates of this theoretical function are rather stable through the complete phase. The model does still not have a good physical interpretation, and we have to look at the model as just a mathematical fit. The second decay rate support the conclusion that the properties of the uppermost phase does not change considerably as we go downwards in the sample, and a major difference in the decay rate is observed when we pass

the first visible phase separating line. This would indicate bigger particles in this lower phases.

6.2 Possible improvements

The attempt to do small angle scattering with the same experimental equipment as for 90° scattering as presented in «The small angle scattering experiment» on page 44 failed. Thus we are not, based on this report, able to say anything about the q -vector dependence in the correlation function. As described in the theory chapter, an investigation of this dependence would tell us more about the structure factors $S_l(k)$ of the correlation function, and hence give more detailed information of which part of the correlation data is related to rotational diffusion and which part to translation. The single 90° scattering does not provide enough data, since the clay system is most probably not like any of the theoretical systems described previously. To improve the correlation data of the suspension it is hence desirable to collect correlation data for a wide range of scattering angles. This may be done by commercial equipment provided such as the goniometer.

Another improvement in the data analysis is to fit the data to a more physically explainable function. The two exponential function fit is rather good for the lag time range from $2E-7$ to $2E-2$, but does not have any good physical interpretation. It is impossible to imagine the clay suspension ruled by only two dynamic decay rates. First of all because the system probably contains more than two distinguishable sizes. As we can see from the AFM pictures a variety of sizes is present. Secondly there must exist decay rates due to rotational diffusion, since the size of the particles is in a range making the condition $qR_g \ll 1$ not valid. Whence there exist a range of decay rates not related to translation. It would be interesting to fit the data to different distributions of decay rates more systematically. As we have seen from Figure 4–11 on page 43 the correlation data also is fitable to a gauss distribution of decay rates. The parameters for this fit are not optimized at all and are just based on trying and failing. A complete fitting procedure using such a distribution is however not trivial since the integral must be solved numerically, and it demands a more thorough investigation of the conditions. In the limit of this diploma work I was not able to do this.

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Appendix A:C program, running the correlator

The program presented is the program used to run the correlation experiment. The program uses some procedures which may be found in the attached floppy-disk, together with a “make-file” which compiles the program.

```

/* correlation.c
 * Written by Erlend Gudding 02.02.00.
 *
 * A program for controlling the correlation card.
 * The correlator is in this program connected to COM1
 *
 *
 * Remember to configurate the serial port before running it.
 * This is done with the command:
 * stty 9600 cs8 -parenb -cstopb ixon -crtcts -echo igncr < /dev/ttyS0
 *
 * For more information on the stty command see the manual entry.
 * (type man stty to your shell)
 */
#include <stdio.h>
#include <unistd.h>
#include <sys/time.h>
#include "step.h"

char *COM1 = "/dev/ttyS0";      /* Linux "name" for COM1 */

/* Please set the values below:*/
int direction=1;                /* Platform: Up = 0; Down =1 */
int step_n = 800;               /* The range of platform adjustment pr correlation*/
/* 1 mm =400 step */
int steps= 4;                   /* The number of correlations totally */
int correlationtime= 315;       /* How long each correlation lasts in seconds*/
char *potential="light.txt";    /* File where data from direct beam intensity is
saved*/
/* End of settings */

/* Defines the function which read the direct beam intensity*/
float multimeter();

/* The programme start*/
int main()
{

    /*Variable settings*/
    int i;

    float value;                /* The value from the multimeter*/

    /* Declarations for the SerialPort */
    FILE *inport;                /* Inn data */
    FILE *outport;               /* Out data */
    FILE *direct;                /* Out data to the potential file*/

```

```

/* open the serial port for reading and writing from the correlator */
inport = fopen(COM1,"r");
outport = fopen(COM1,"w");

/* Check if the serial port is opened */
if (inport == NULL || outport == NULL)
{
    printf("Could not open the port: %s\n", COM1);
    return -1;
}

/* Opens the file which direct beam intensity data is saved */
direct=fopen(potential,"w");

/*Start the correlation routine which is done 'steps' times*/
for(i=0;i<steps;i++)
{
    fputs("run\n", outport);

    sleep(correlationtime); /* Wait untill the correlator is finished*/
    value=multimeter();      /* Reads the multimeter */
    fprintf(direct,"%0.4f\n",verdi); /* Save the value to a file */

    /*The following initialize the parallell port and turns the motor of
step_n*/
    /* Set the communication to paralell port LP1 */
    int port = LP0_PORTBASE;

    /* Get permission to use the port, must be done before turning the
motor */
    if(ioperm(port, 1, 1) == -1)
    {
        printf("No success (port busy?)\n");
        return 1; /* The program is determined */
    }

    /* Turn the motor 'step_n' steps */
    step(port, step_n, dir);

    /* End the paralell communication */
    ioperm(port, 1, 0);
}

/* Close the file for saving direct beam intensity */
fclose(direct);

/* Close the serial port */
fclose(inport);
fclose(outport);

return 1;
} /* End of the main program */

```

Appendix B:Format converting C program

The program below is used to convert the ASCII-data files produced by the ALV-5000 correlation program. The respective lag time datafile “timtab” containing the lag time information is found in the attached floppy disk.

```

/*
 * Written by Erlend Gudding for gcc under Linux. Jan 2000
 *
 * The program converts the correlation data saved by the alv-5000
 * into a ASCII table where the time data is stored in the first column
 * and the correlation data in the second column. The two column is
 * separated by a blank char.
 *
 * It is necessary to have a data file for the correlation lag times, tau.
 * This data is present in the file 'timtab'.
 *
 * The syntax for the converting is:
 * Filformat 'Oldfile' 'Newfile'
 * where 'Oldfile' is the original data file, and 'Newfile' is the file
 * you want to put the converted data. 'Oldfile' and 'Newfile' may have
 * the same name.
 */

#include <stdio.h>
#include <stdlib.h>

#include <string.h>
#include <stddef.h>
#include <time.h>

/* The Main program */

/*variables*/
FILE *fp, *table, *newfile;

const int MAX1=10000;
const int MAX2=10000;
const int MAX3=10000;

/* Defines the pointers to the file to convert and the converted data
char *targetfile, *outfile;

int x;
int c=0;
int t=0;
int o=0;
int n;
int cnt;

int main(int nargs,char *args[])

```

```

{
/* Set some control characters*/
char *innsett ="b";
char test;
char corr[MAX1];
char time[MAX2];
char outdata[MAX3];
char *lineshift="\n";
char *blank=" ";
int i;

/* Allows you to write the target and result right after the command*/
targetfile=args[1];
outfile=args[2];

/* Open the target file for reading and writing */

fp = fopen(targetfile,"r");
table = fopen("timtab","r");

if (fp == NULL)
{
printf("Could not open the file: %s\n", targetfile);
return -1;
}
if (table ==NULL)
{
printf("Could not open the file: %s\n","timtab");
return -1;
}

/*Read the target file into a table */
for (cnt=0; cnt<(MAX1-1) && fscanf(fp,"%c", &corr[cnt])==1;cnt++);

fclose(fp);

/*Read the time data file 'timtab' into a table */
for (cnt=0; cnt<(MAX2-1) && fscanf(table,"%c", &time[cnt])==1;cnt++);

fclose(table);

/* initialise start */
while (time[t]==*blank)
t++;

while (!((corr[c]=='C')&&(corr[c+1]=='O')&&(corr[c+2]=='R'))
c++;
c=c+26;
while (corr[c]==*blank)
c++;

```

```

/* Putting only the right values a into a outdata table */
while (corr[c]!='R')
{
    /* Put in the next time value */
    while ((time[t]!='blank') && (time[t]!='lineshift') && (time[t]!='13'))
    {
outdata[o]=time[t];
o++;
t++;
    }

    /* Puts in a blank char between time and correlation data*/
    outdata[o]='blank';
    o++;

    /* Puts in the next correlation data value */
    while ((corr[c]!='blank') && (corr[c]!='lineshift') && (corr[c]!='T'))
    {
outdata[o]=corr[c];
o++;
c++;
    }
    /* Puts a lineshift char to create a column */
    outdata[o]='lineshift';
    o++;

    /* Prepare for the next number for time and correlation*/
    while ((corr[c]=='blank') || (corr[c]=='lineshift'))
        c++;
    while ((time[t]=='blank') || (time[t] == 'lineshift') || (time[t] == 13))
        t++;

}/* End of the proc. creating the new table*/


/* Saving the new data from buf3 to newfile */
newfile = fopen(outfile,"w");

for (n=0;n<o;n++)
    putc(outdata[n],newfile);

/* Close the files for reading and writing*/
fclose(newfile);

} /* End of the converting program*/

```


Appendix C:Data analysis.

To analyse data a main task is to fit the collected data a theoretical curve or function. A lot of programmes today do this automatically, but in order to understand some of the calculations they do and to evaluate the legitimacy of the results this chapter will in short terms concern how the Microcal Origin do the fitting procedure.

First of all, after a plausible theoretical function is chosen, the fitting procedure starts to minimize the difference between the parametric function and the experimental data [20] . A common way to do this, which also is the way Origin does the fitting is to minimize the sum of the squares of differences between the function value and the data points for all the data:

$$\chi^2(p_1, p_2, \dots) = \frac{1}{(n^{eff} - p)} \sum_i w_i (y_i - f(x_i, p_1, p_2, \dots))^2 \quad [C.1]$$

This new function is called chi-squared and is a measure of how well the parametric function $f(x_i, p_1, p_2, \dots)$ is fitting the data points y_i . $p_1, p_2, \dots$ is the parameters in the fitting function and as long as one can adjust these parameters and reduce the chi-squared, a better approximation is reached. The pre-factor w_i a weighing factor if we want to favour some of the data points. Now the Jacobian is computed as

$$F_{i,j} = \partial f(x_i, p_1, p_2, \dots) / (\partial p_j), \quad [C.2]$$

and the variance-covariance matrix is computed as

$$C = (F' \otimes F)^{-1}. \quad [C.3]$$

The standard error of parameter i is now defined as $\sigma_i = \sqrt{C_{ii}\chi^2}$. The fitting steps are done by using a Levenberg-Marquardt (LM) iteration, and the parameters are adjusted until the χ^2 of the fitting function is closer to the data set than a fixed tolerance limit.

Before starting the fitting procedure, we have to give the parameters initial values. If these values are set too far from the true value, the LM-iteration diverges. Hence it is necessary to find approximated values of the parameters before we start fitting.

Appendix D:MatLab script

The computer script below is used by MatLab to compute a theoretical correlation function for a system of a gauss distribution of decay rates. The gauss distribution is given as

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right\}. \quad [\text{D.1}]$$

The mean decay rate for the computations below is 1,5 ms and the variance of the distribution is 0,6 ms. The integral computed below is then

$$G(\tau) = \int_{Low}^{H\ g n} f(\tau_1) \exp(\tau/\tau_1) d\tau_1. \quad [\text{D.2}]$$

The following short MatLab script was executed to do the numerical calculation:

```
mean=1500;
var=600;
tau=( [1:(4*var)]+mean-2*var)*1E-6;
dx=1E-6;

int=zeros(size(t));
for i=1:size(t)
    temp=0;
    for j=1:4*var
        temp=temp+exp(-0.5*((tau(j)-mean)/var)^2-(t(i)/(tau(j))))*dx;
    end;
    int(i)=temp;
end;
c=int(1);
int=int/c;
```

The script need in addition an array, t, of the lag times we want to generate the correlation function for.

The program is, as we can see, quit short but the computation time is still long and is increasing with increasing variance and better solution of the integral.

The script is also found in the floppy-disk attached.

