

Dynamical behavior of soft colloidal nanoglasses

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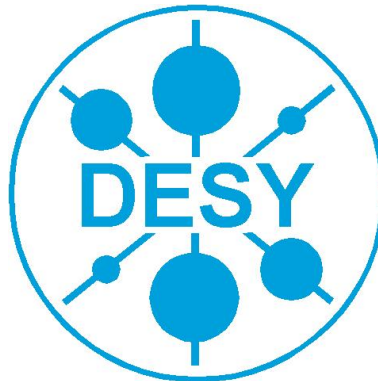
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September 7, 2012



Abstract

In this experiment, carried out in the framework of DESY Summer Student Program 2012, a soft colloidal suspension consisting of polymeric PNIPAM particles in water was synthesized and after was investigated by dynamic light scattering techniques. The radius of the particles in suspension was found in the liquid phase and the thermal responsivity of this kind of particles was verified (see [3]). The size of these particles matched the expected values according to the proportions of the reagents used in their preparation. For the glassy phase the relaxation time of the system was found, while some aging problems were detected. The dynamical susceptibility of the system showed typical glass behaviour. Colloidal suspensions are a good model for researching dynamics at nanoscale, specially the glass phase transition. The results of this experiment could act as a model for molecular solids, liquids and glasses.

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1 Introduction

The main goal of these experiments is to become familiar with the study of colloidal suspensions by means of dynamic light scattering techniques, especially in glassy and liquid phases. The experiment is divided in three steps. First the colloidal system will be synthesized and prepared for study. After that, the sample is analyzed in a diluted form -liquid phase- so the radius of the particles in colloids can be calculated. Finally the system will be taken in its concentrated form -glassy phase- and its dynamics will be thoroughly researched.

2 Theory

In this section the theoretical basis for all the experiments is explained or referenced. It is not possible to build from scratch the entire formal apparatus of all the physical laws involved in this study. Therefore most of the theorems and results used for reaching conclusions will be just stated briefly and further references about them will be added nearby.

2.1 Poly-N-isopropylacrylamide (PNiPAM)

Colloidal suspensions are constituted of microscopic-sized particles in liquid, and they are useful as a model system for studying the glass transition because the particle motion lies on an experimental accessible time scale. A well-known polymeric chain used as an instance of soft colloid -in opposition to hard colloids- is PNiPAM.

Aqueous dispersions of Poly-N-isopropylacrylamide (PNiPAM) consist of thermosensitive polymeric particles which are dispersed in distilled water [3]. The molecular structure of PNiPAM is presented in figure 1:

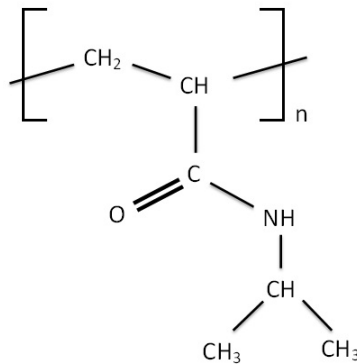


Figure 1: Schematic structure of molecular PNiPAM

Colloidal particles have temperature-dependent behavior in water and size of the particles immediately collapse at 32°C, known as volume phase transition temperature (VPTT) (see figure 2). PNiPAM is hydrophobic above VPTT and expels water. Upon heating, the reflective index, permeability, chemical potential and volume fraction of the particle also change. Below the VPTT it becomes hydrophilic

and particles are swollen and accordingly show a high permeability so that the chemical potential and refractive index of water match inside and outside particles.

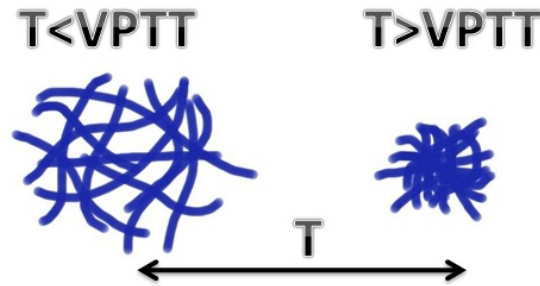


Figure 2: Temperature dependent particle size of PNiPAM. Swollen particle (left), collapsed particle (right).

Another interesting phenomenon is that the PNiPAM dispersion exists in three phases (liquid, crystal and glass). Each phase can be obtained by changing the temperature or weight-percent. The phase behavior of PNiPAM-co-allylamine particles with slightly higher volume phase transition temperature around 35 °C is presented in figure (3).

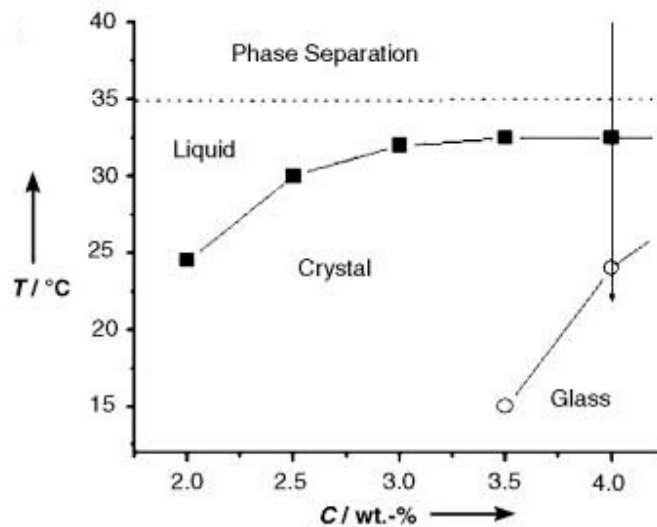


Figure 3: Phase diagram of aqueous PNiPAM solution from [1]

2.2 Light Scattering Methods

Light scattering is a widely used technique for the characterization of particle size in colloidal suspensions. It consists on a beam of coherent and monochromatic light which is scattered by a thin sample in its way. The intensity of the scattered light is then measured at some chosen angle. Since the particles in diluted sample (non-interaction particles) are undergoing constant Brownian motion we are dealing with quasi-elastic light scattering. In this case $|k_{out}| = |k_{in}|$, where k_{in} and k_{out} are wave vectors of the incoming and scattering light accordingly. Figure 5 illustrates the scattering geometry.

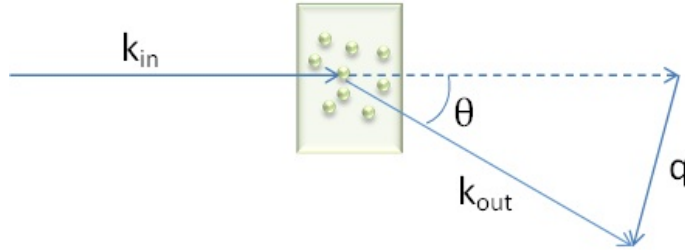


Figure 4: Schema of the scattering geometry

q is the scattering vector, which is defined as

$$q = k_{out} - k_{in} \quad (1)$$

$$|q| = \frac{4\pi n}{\lambda} \sin(\theta), \quad (2)$$

where n is refractive index of the solvent and θ is the scattering angle.

Brownian motion leads to the fluctuation of the intensity. Dynamic Light Scattering can be used for measuring the temporal intensity fluctuations in the diffraction speckle pattern caused by colloidal suspensions. In these experiments we use correlation methods to analyze the scattering data. This is typically done by means of the normalized intensity autocorrelation function (ACF):

$$g_2(q, \tau) = \frac{\langle I(q, t) I(q, t + \tau) \rangle_t}{\langle I(q, t) \rangle_t^2} \quad (3)$$

where $\langle \dots \rangle$ denotes time averaging, τ is the lag time.

More information about autocorrelation function and other mathematical tools present in dynamic light scattering technique can be found in 2.

By the normalized field autocorrelation function $g_1(1, \tau)$ via the Siegert relation the measurable quantity $g_2(q, \tau)$ provide access to actual physical microscopic properties

$$g_2(q, \tau) = 1 + \beta |g_1(q, \tau)|^2, \quad (4)$$

where the coefficient β depends on the detection optics. Conventional laser light shows a nearly perfect coherence with $\beta \approx 1$

Under Brownian motion the normalized field correlation function can be written as

$$g_1(q, \tau) = \exp(-\Gamma\tau) = \exp(-\tau/\tau_c) \quad (5)$$

with $\Gamma = D_0 q^2$ being the relaxation rate and $\tau_c = 1/\Gamma$.

D_0 is the particle diffusion coefficient defined by the Stokes-Einstein relation:

$$D_0 = \frac{k_B T}{6\pi\eta R_h} \quad (6)$$

where k_B is the Boltzmann constant, η is the solvent viscosity, T is the temperature and R_h is the hydrodynamic radius.

The last equation is widely used in DLS for determining the radius of small particles.

When using the CCD camera, the time average in the ACF is replaced by an average over pixels:

$$c_I(q, t, \tau) = \frac{\langle I(q, t_1) I(q, t_2) \rangle_p}{\langle I(q, t_1) \rangle_p \cdot \langle I(q, t_2) \rangle_p} \quad (7)$$

The importance in this new expression lies on the fact that averages are not on temporal scales but over all the pixels in one picture, as each pixel is considered as an independent detector. The autocorrelation function $g_2(q, \tau)$ is just the time average of the two time correlation function:

$$g_2(q, \tau) = \langle c_I(q, t, \tau) \rangle_t \quad (8)$$

Characterizing the temporal fluctuations of c_I by means of its variance will lead to the dynamic susceptibility χ . This function, for glassy phases, is expected to be a peak centered in the relaxation time of the system, the sought after parameter in this experiment.

3 Experimental method

Here, the experimental set-up and procedure used in the acquisition of the necessary data are presented and exhaustively explained.

3.1 Synthesis of aqueous PNiPAM nanogels

Monodisperse N-isopropylacrylamide (NIPA)-co-allylamine colloidal spheres were synthesized by using a radical polymerization method. This is a list of the substances and their amounts which are necessary for the synthesis, to get spheres of radius of order 10×10^{-8}

- N-isopropylacrylamide monomer (NIPAM) (19.2212 g)
- Methylenebisacrylamide (MBAm) (0.6580 g)
- Allylamine (1 g \approx 1.332 mL)
- Deionized water (1175 mL)
- Natriumdodecylsulfat (NLS) (0.3780 g)
- Sodium sulphite (0.1090 g)
- Potassium persulfate (KPS) (0.1353 g)

Weighing all of these substances was made with a precision balance (precision of ± 0.0001 g). The monomer NIPAM, MBAm, allylamine and the deionized water were mixed in a three-necked flask. The magnetic stirring was used in order to dissolve all the substances in the water. Before activating the stirring mechanism, a nitrogen supplier was connected to our system for removing the oxygen present on it, and also a water cooling system was used to prevent solution from boiling. This solution was heated up to 50 °C.

Simultaneously potassium persulfate was mixed with 5 mL water and the same stirring technique was used to dissolve it. After half an hour, when the potassium persulfate was totally decomposing, it was added to the previous mixture for initialize polymerization.

The reaction was maintained at 50 °C under nitrogen for 5 hours. After cooling the resulting particle dispersion was filtered out in order to remove impurities. Then, it was placed inside a dialyzer membrane and under deionized water, to brush away the undesired ions by osmosis. Water was replaced every day, during one week, to accelerate the process.

The dialyzed particle dispersion was reconcentrated several times. This was accomplished by a rotating evaporator assembly, which makes use of a warm water bathing and a pressure reduction by a vacuum pump.

Using the high precision balance, we calculated the weight-percent concentration by measuring the sample before and after evaporating the water on it in a vacuum oven.

We used the next expression to calculate the wt%

$$\frac{WA - WT}{WB - WT} \cdot 100\% \quad (9)$$

where WT, WA, WB are the tara's weight, weight of the sample before evaporation and after accordingly.

3.2 Light scattering setup

The schematic setup of the DLS is given in Figure 5.

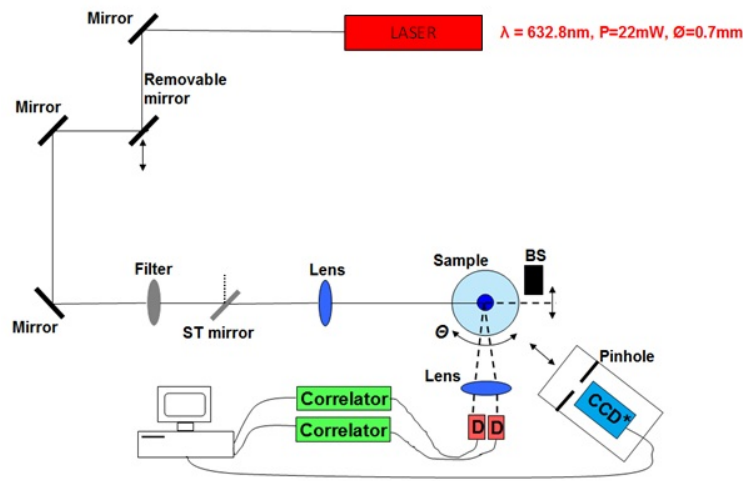


Figure 5: Schematic setup of laser light scattering instrument

Parameter	HE-NE laser
Wavelength λ	632.8 nm
Power P (TEM_{00})	22 mW
Beam diameter ($1/e^2$)	0,7 mm
Beam divergence	1.15 mrad
Polarization ratio	500:1 (vertical)

Table 1: Laser parameter

This experiment made use of 3D DLS spectrometer from LSI instruments. Two avalanche photodiodes (APDs) were fixed on the goniometer arm. The goniometer arm can be placed at an angle between 20° and 150° . The extended setup consists on the light source that is represented by the He-Ne laser which specifications are shown in the following table. (1)

Before beam from He-Ne laser reaches filter systems it has deflected four times. Two filters decrease the incoming laser intensity and these systems are mounted very close to the laser head due to the high laser power. Conclusively the laser light is focused by lens into the sample cell and the signal of the scattered light can be measured by APDs or the CCD camera. To overcome parasitic scattering of the sample cell wall, the samples are placed to in a cis/trans-decalin bath, because the refractive index close to all substances used in the experiment, and therefore minimizes the deviation due to refraction. To set and control the temperature a Julabo water refrigerated/heating circulator (Julabo Labortechnik GmbH, Seelbach/Germany) is connected with the decalin bath. The APDs are used to measure the hydrodynamic radius of the diluted PNiPAM samples. For researching the glassy phase we use a CCD camera in an analogous way. The most important difference is that the camera acts as an area detector, on one side, and on the other, that the parameter of time exposure for each frame recorded can be changed. Therefore, the rate of the camera can take values from 1 fps to 120 fps. This feature will prove to be crucial when adapting our recording to the time scale of dynamic behaviour in glasses.

4 Results, data analysis and discussion

The results of our experiments with its subsequent discussion are presented in this section, organized accordingly to the three different parts stated above.

4.1 Synthesis of aqueous PNiPAM nanogels

The procedure was carried out with no incidences.

In table 2 weight results are presented:

N	Tara weight [WT] (mg)	Weight before ev. [WB] (mg)	Weight after ev. [WA] (mg)
Sample 1	12784.4 ± 0.1	15263.1 ± 0.1	12826.2 ± 0.1
Sample 2	39758.6 ± 0.1	41798.3 ± 0.1	39872.6 ± 0.1
Sample 3	39759.1 ± 0.1	39942.2 ± 0.1	39778.6 ± 0.1

Table 2: Weight measurements for tara, sample before and after evaporation.

We obtained, for sample 1, $1.686 \pm 0.006\%$, for sample 2, $5.589 \pm 0.007\%$ and for sample 3, $10.651 \pm 0.006\%$

4.2 Measure of PNiPAM radius at different temperatures

In this section, the radius of PNiPAM and SiO₂ (silica gel) is measured at different temperatures in order to detect the temperature responsive behavior of the first one. SiO₂, a well-known colloidal suspension, is used as a control sample. The diffraction assembly was set in a scattering angle of 90°. Then, the refrigerator was used to cool down the receptacle where the sample was kept down to the desired temperature. This magnitude and the exact angle were read using the computer *3DDLS* software directly. Laser was switched on and a period of one hour was left before starting the measures so as the beam could stabilize. Then, the measures began. Each measure was carried out for 120 s. and then the temperature was increased with the refrigerator. The next measure did not start until the temperature was stabilized. Nevertheless sometimes variations of ± 0.03 K were observed during the data recording, which we consider to be despicable.

Also the intensity of the incident light was changed whenever it went above 400 kHz, as therefore

the APDs reaches the electronic flow limit, and the measured intensity is not reliable. To do that, a set of different filters of unspecified power was used, which granted us a beam with intensities between 100 and 400 kHz.

Here we show a figure of the obtained self-correlation functions from the data recorded.

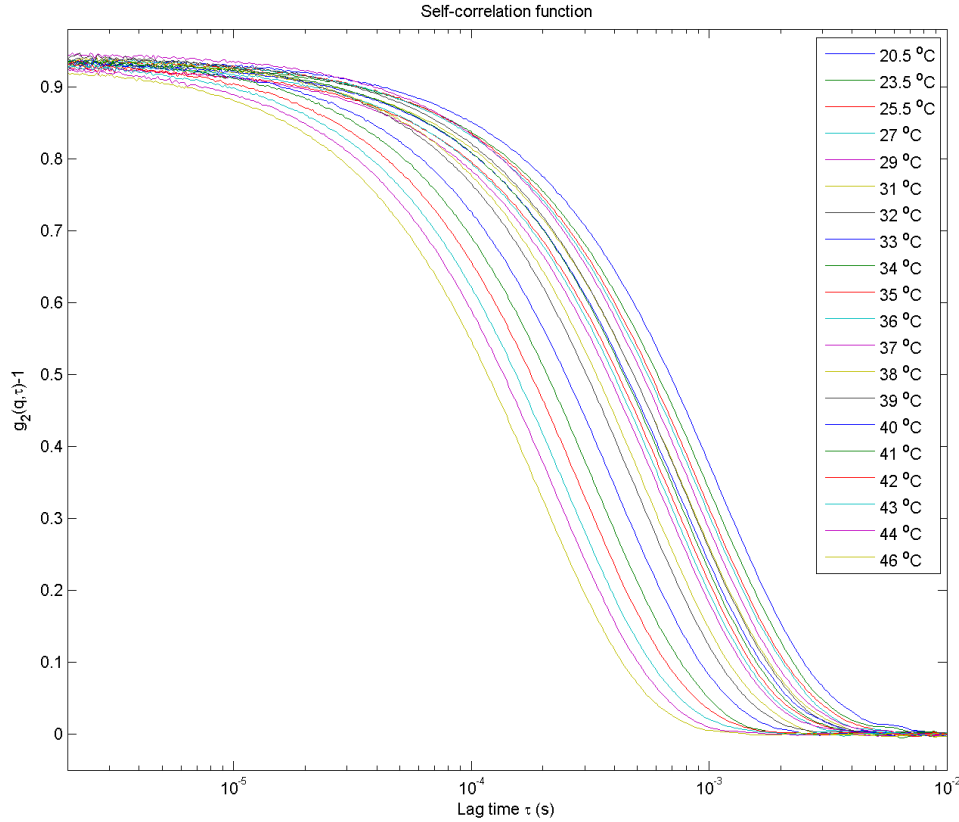


Figure 6: Trasversal outline of the beam trajectory

Note that the bigger temperature allows for a faster decay, as the particles are more excited, therefore the velocity of the system is increased, and it is reasonable to think that changes occur faster.

With this value, and the given values for the viscosity, we can also calculate the hydrodynamic radius of the particle, using expressions in . To contrast this values, we repeat the same procedure for the SiO_2 samples. The final result is the following graphic:

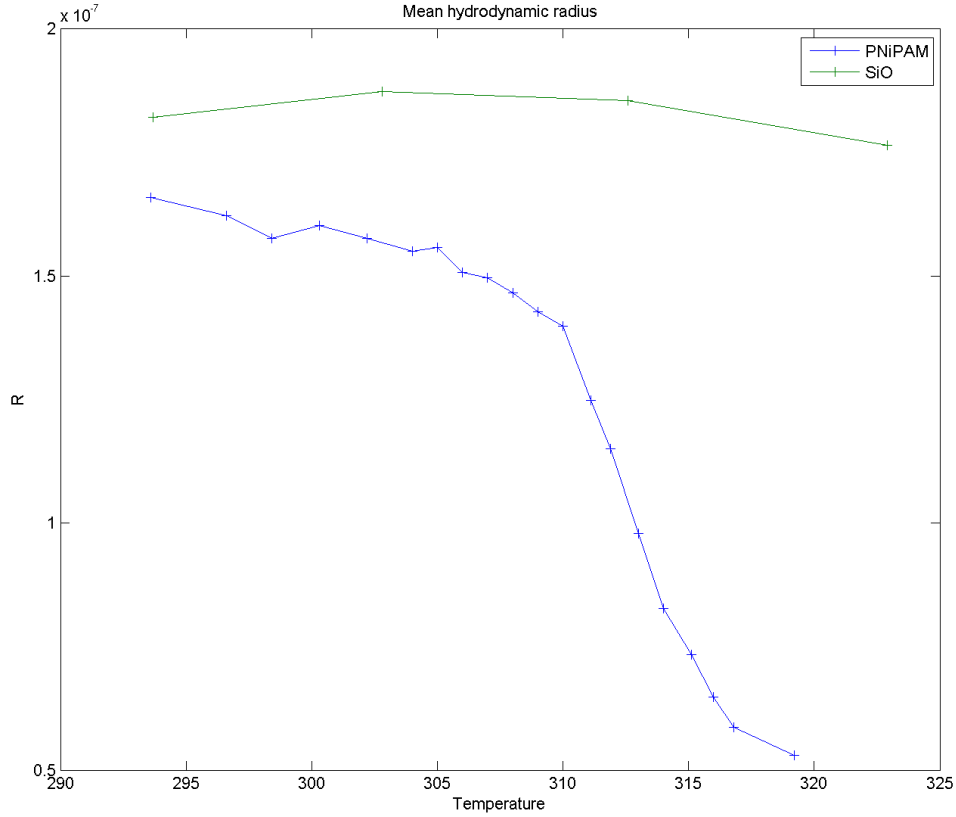


Figure 7: Transversal outline of the beam trajectory

A fast reduction in radius at some rank of temperature is easily seen, due to the thermal responsivity of the particles. More measures could have been taken in higher temperatures to see if the radius remained constant again, but it is dangerous to let the temperature of PNIPAM approach 50 °C, as therefore the polymer is spoiled with no turning back. We see, nevertheless, that there is not much difference between radius at 44 ° and at 46 °.

4.3 Glassy phase dynamics study

Many different measures were carried out in this section. The apparent lack of results became a powerful reason to repeat the experiment for several dozens of times. Although the sought goal was finally accomplished, new questions arise at the sight of final results.

4.3.1 Measuring sample of 6 wt %

First measures were carried out for a sample prepared at a concentration of 6% from our most concentrated sample DD_2 . Measures were taken using different exposure times for the camera, at frame rate acquisition of 1, 5 and 120 frames per second. The resulting two time correlation function was very similar in all cases, as we can see in next picture:

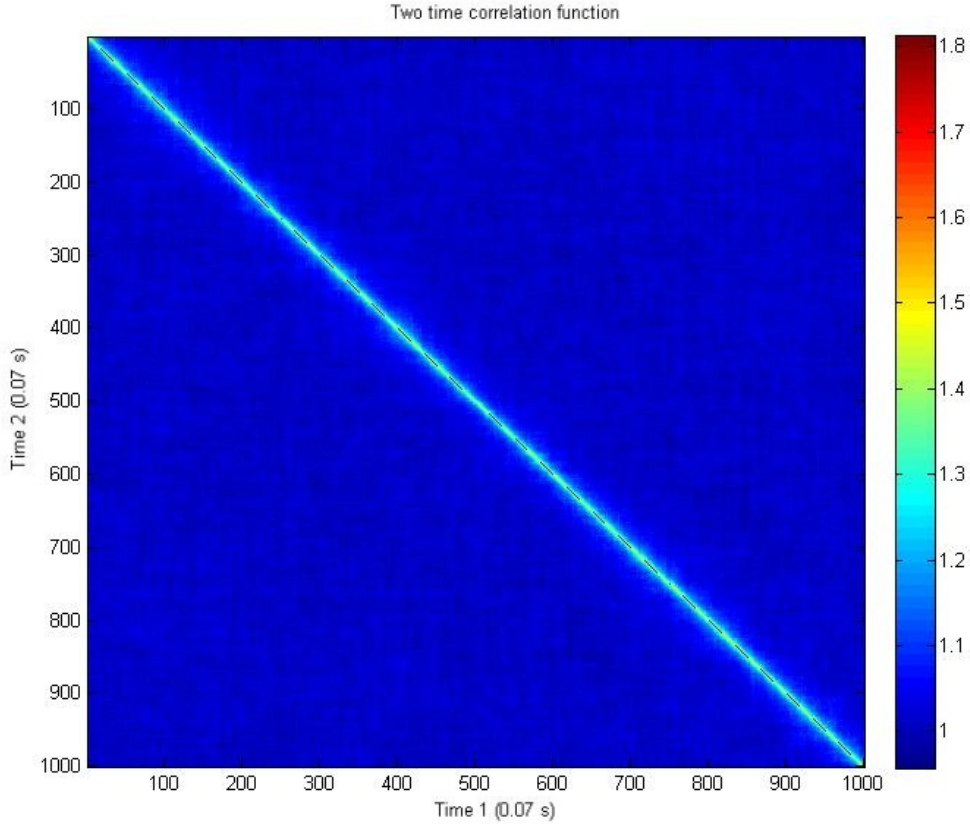


Figure 8: Two-time correlation function for sample at 6 %, 120 fps, $\theta = 30^\circ$

Even using the fastest acquisition frame rate, it was not possible to resolve the dynamics of the system, as the decay in the correlation occurred too fast. Therefore, the decision of using a more concentrated sample was taken, instead on going with further analysis on this sample. This way it would be possible to have a slower system.

4.3.2 Measuring sample of 10.6 wt %, quartz bottle

Next measures were made using directly a sample of *Sample 2* from table 2 in a quartz bottle specially designed for dynamic light scattering experiments.

First experiment was performed at 120 fps. The resulting two-time correlation ended like this:

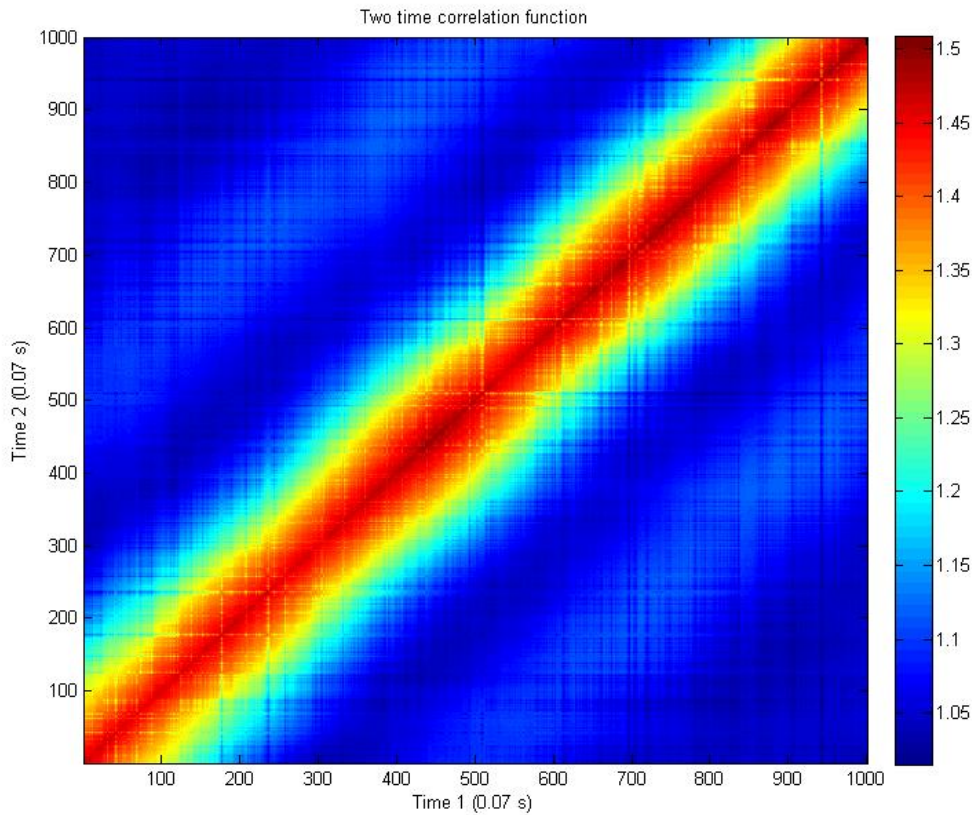


Figure 9: Two time correlation function for 120 fps, sample at 10.6 %, quartz bottle

The autocorrelation function and the dynamical susceptibility were not acceptable due to the excessive velocity of the frame rate. That led us to being unable to resolve the system in our time. Furthermore, some time passed since the sample was set-up and the experiment started, and later it will be shown that this affects the two time correlation function.

Latter experiments, nevertheless, only displayed a massive correlation behaviour, which can be seen in next figure. Similar pictures were found for other fps, from 1 to 120.

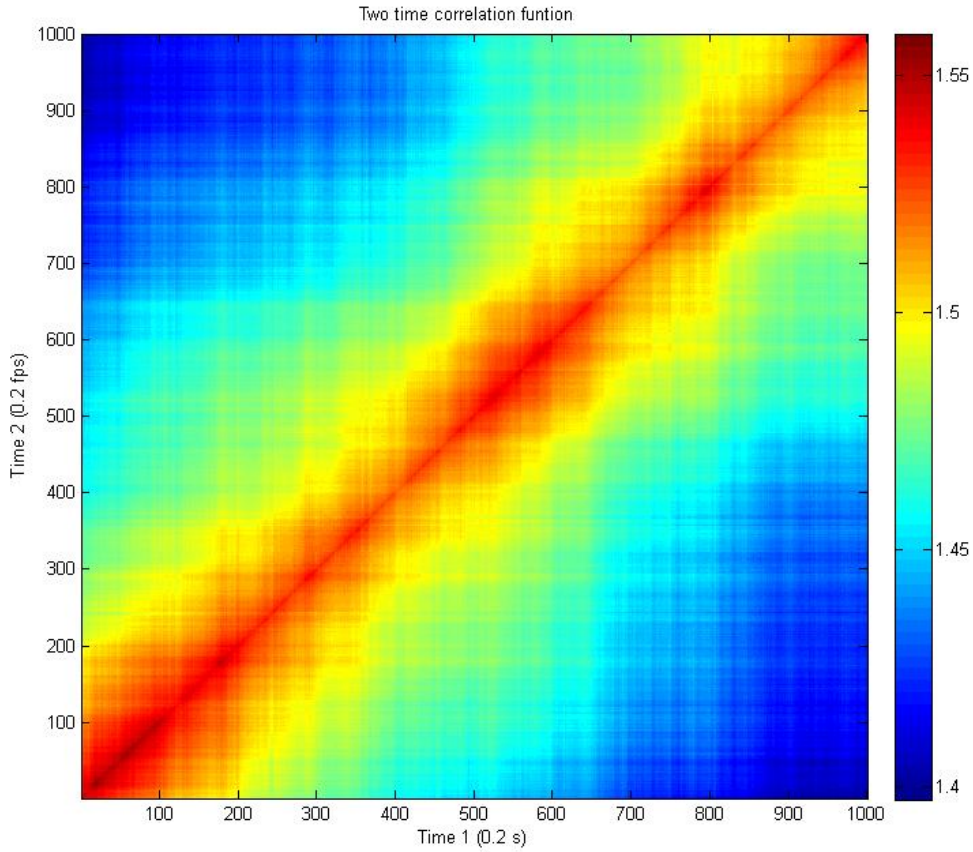


Figure 10: Two time correlation function for 5 fps, sample at 10.6 %, quartz bottle

Then the sample was taken out of the experimental set-up for some time, not on purpose, and then put back again in the path of the laser beam. The resulting figure obtained is shown next; it proved to be of high interest to show the real behaviour of the system, and it is the clearest image of the changes in time of the system.

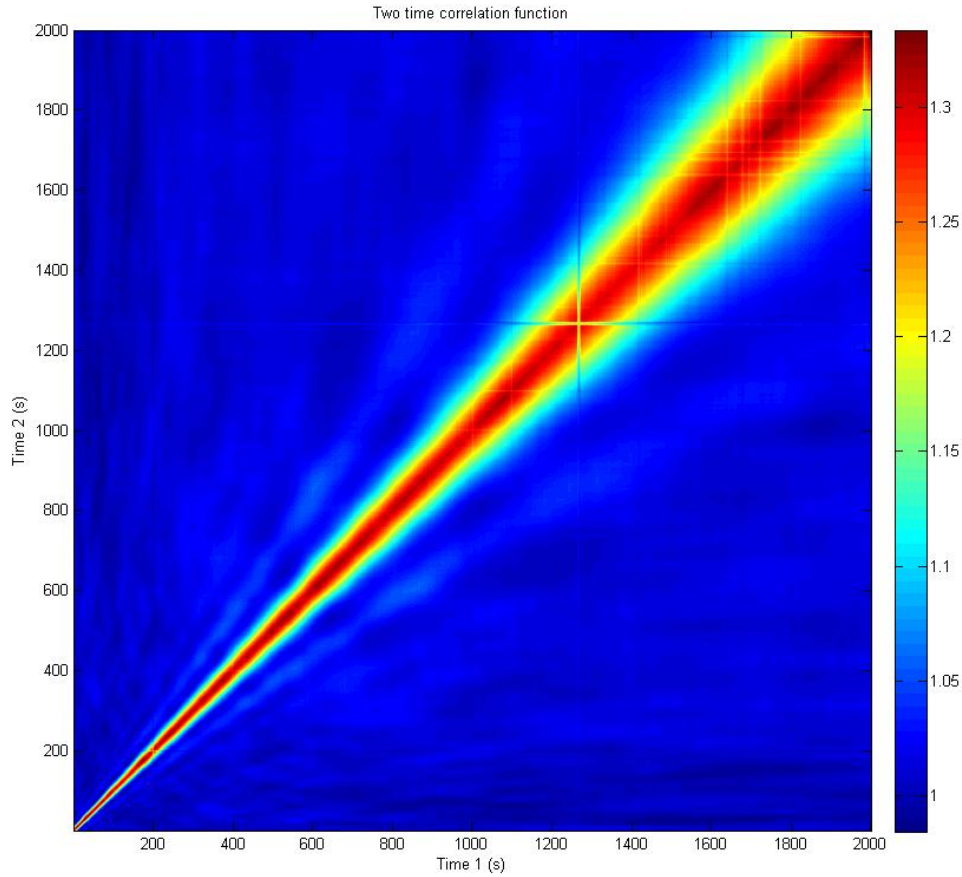


Figure 11: Two time correlation function for 5 fps, sample at 10.6 %, quartz bottle

After that, figures were again too much correlated, like in figure 10. At that moment the meaning of such changes was not understood, but under the light of all the results measured, we can explain the obtained results using a summary which attempts to explain all the collected results.

Rate of frame acquisition has a big influence over the final display of two time correlation function. When frame rate is increased to its maximum, it is possible to look at the system at very fast time scale. Nevertheless, if the system is too fast, correlation is only found in the diagonal line of this figure, but the rest of the system is totally uncorrelated, as in figure 8. If frame rate is well chosen, the resulting figure resembles 9. If the system is too slow for that frame rate, the correlated diagonal in the two time picture becomes wider, and it can even fill all the picture, as in figure 10. Therefore it is possible

to identify a qualitative variable: the width of the diagonal in the two time function. If the system is too fast compared to the rate of picture acquisition it is small. On the contrary, if it is too wide, the conclusion is that the system is too slow.

Now, back to the experiments, it is possible to see a broadening diagonal in figure 11, which means that the system is slowing down in a fast way. That also agrees with the fact that for the second and further measures on the quartz bottle sample the system appears to be very slow: no matter what fps is chosen, even with the slowest fps of 1, the system is too slow to reach correlation decay between first and last shots.

This behaviour is somehow reset when the set-up is changed, by means of an angular rotation or replacing the sample for a different one which contains the same substance and concentration. For example, when changing the scattering angle, results obtained are satisfactory just for the first measure, and then the system slows down again. This behaviour will be attempted to explain later, as it falls out of the scope of the theoretical aspects of glass dynamics studied in this experiment.

Next measures only confirm these suppositions, with no exceptions. Nevertheless it is possible to study the dynamics of the system using only the first set of pictures taken on a recently moved sample. This is shown in the next measurement.

Back to the experiment, suspecting about a multiple scattering problem, the course of action taken was to replace the sample by a 2mm capillary, but then again, we changed our minds and the sample in quartz bottle was put back again on the set-up and measured, and the result was quite satisfactory.

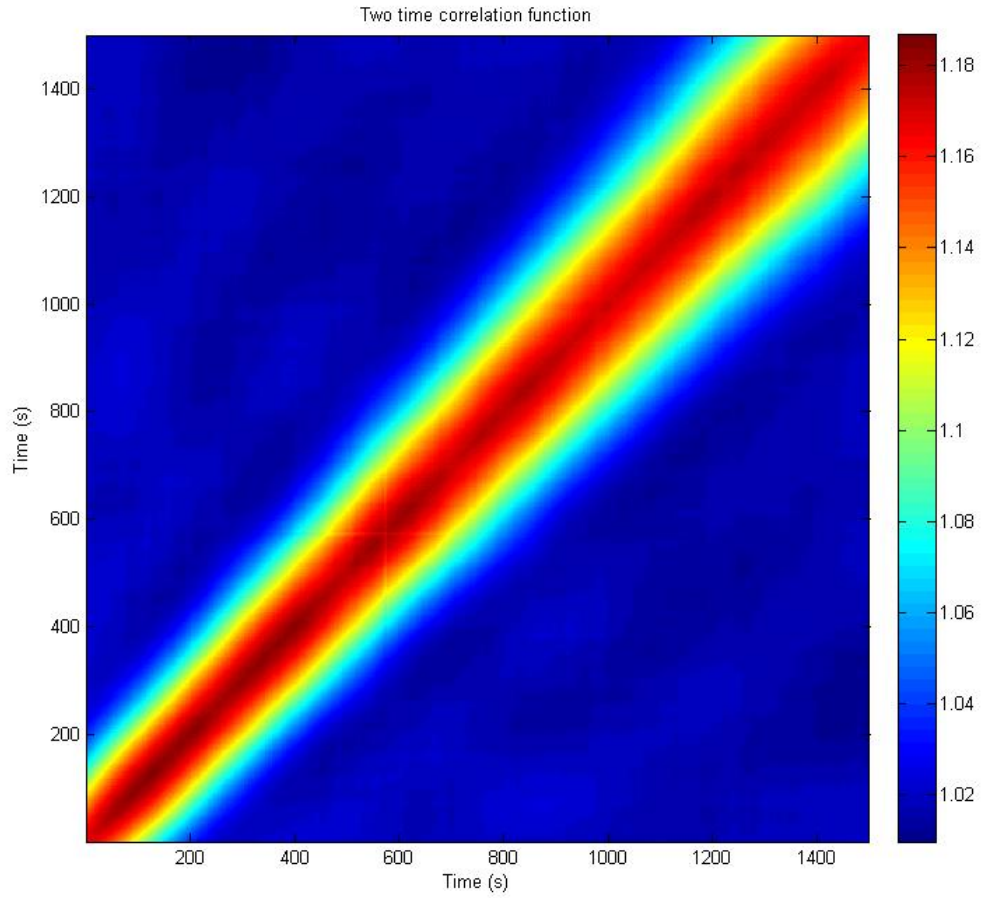


Figure 12: Two time correlation function for 1 fps, sample at 10.6 %, quartz bottle, after moving

Here are the autocorrelation function and the dynamical susceptibility:

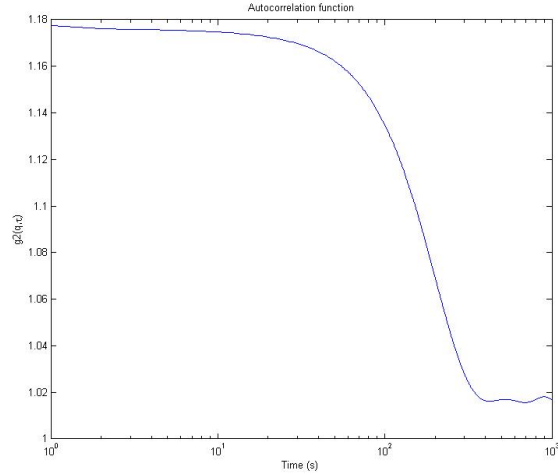


Figure 13: Autocorrelation function for the previ-
ous measurement

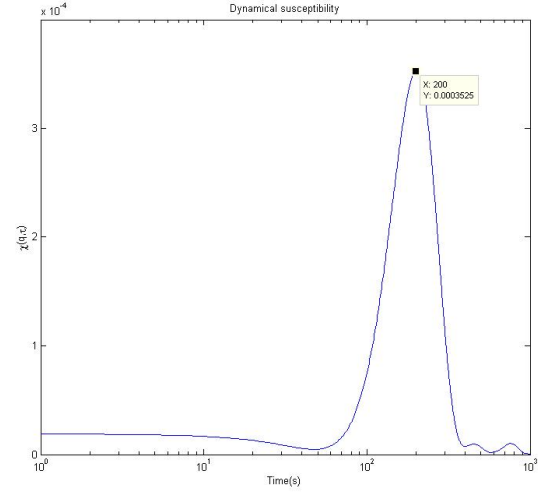


Figure 14: Dynamical susceptibility for the previ-
ous measurement

Results show that the system is found in glassy phase with a relaxation time of $\tau = 200s$.

After this measure all the others displayed bad behaviour such as in 10 as predicted in our aging hypothesis. Finally, it was definitely decided to switch to 2mm capillary.

4.3.3 Measuring sample of 10.6 wt %, 2mm capillary

First measures were good enough to go forward with the complete analysis of the dynamics. This is the obtained two time correlation function.

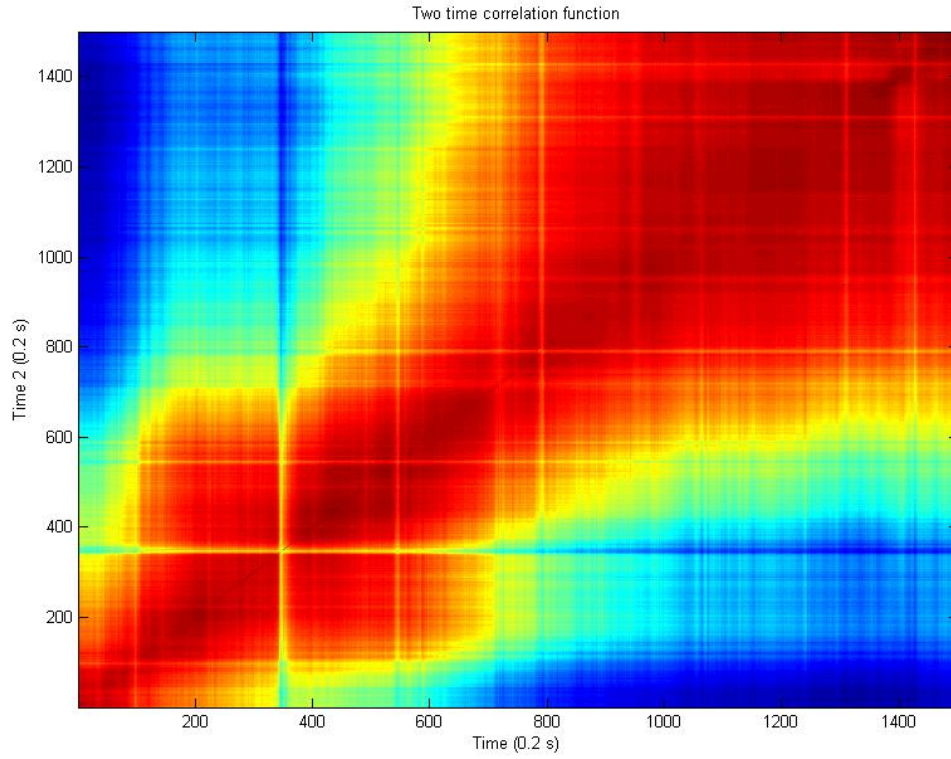


Figure 15: Two time correlation function for 5 fps, sample at 10.6 %, 2mm capillary

Here are the autocorrelation function and the dynamical susceptibility:

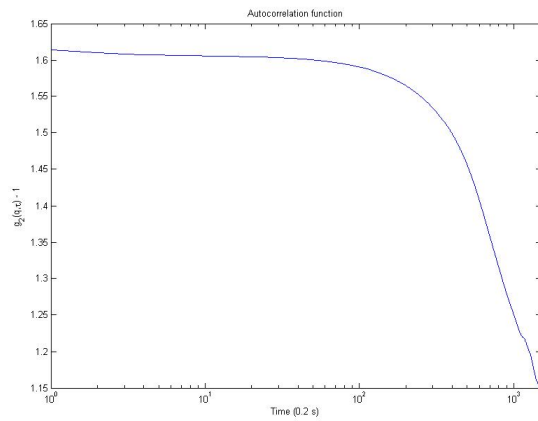
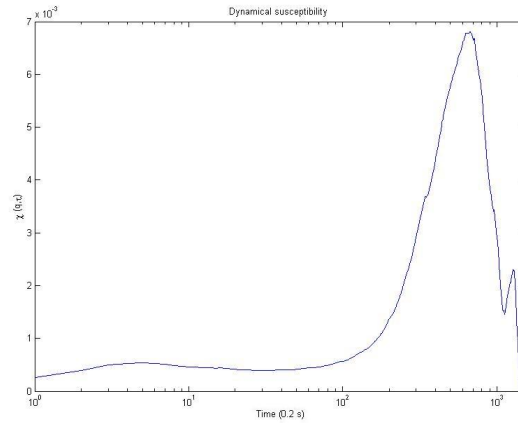


Figure 16: Autocorrelation function for the previ-



ous measurement

Results show that the system is found in glassy phase with a relaxation time of $\tau = 134$ s, which is

not the same that we had before, which can be explained because of the fast changing behaviour of the glass. Nevertheless, the peak shape, in addition to the relaxation time over 100 s. shows that sample is, as supposed to be, in glassy state.

Later, the aging acted on our system and it was impossible to keep on researching on its dynamics. This is the point when we started suspecting about some unknown factor acting in the system and changing it rapidly so as no more than one or two measures could be made.

Therefore an experiment to see clearly the aging effect was set-up and performed. Geometry of the experiment was set up at 30 degrees and fps of 10 was used, which later proved to be too much. Nevertheless, the aging effect is perfectly seen in it. A new 2mm capillary sample was prepared, with the same substance and measured by the usual method. After five minutes the experiment was repeated again without changing any single component of the assembly.

These are the two time correlation functions obtained:

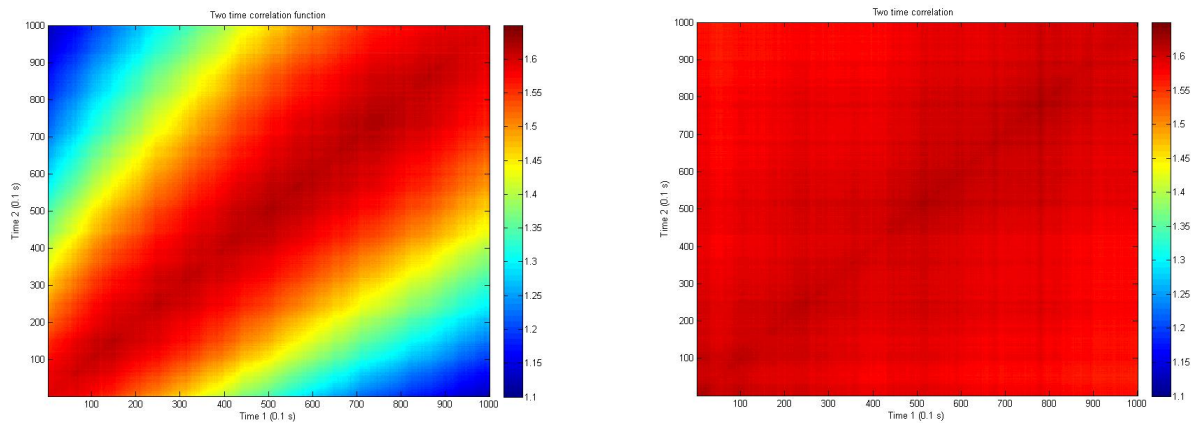


Figure 18: First measure, starting 1 minute after placing sample

Figure 19: Second measure, starting 7-8 minutes after placing sample

Clearly the aging effect becomes evident at our eyes.

Therefore, since the problem lies in system becoming too slow, apparently, another sample is prepared, between the fast motion of 6 % sample and the slow final equilibrium of 10.6 % sample.

4.3.4 Measuring sample of 8 wt %, 2mm capillary

Finding the same problems than for the previous sample, the final decision was to end here the experiment, although an interesting path to follow would be to study again the first sample or use a weight of 7%.

5 Conclusions

This experiment was divided in three different parts: the synthesis of polymers forming the colloidal suspension, the dynamic light scattering scheme used to study the size of the particles in the diluted colloid, and the same assembly used for studying the behaviour of the glassy phase.

The synthesis of the polymer was carried out without any inconveniences, and different samples of the desired colloidal suspension were prepared at different concentrations, therefore different phases, for latter study.

After that, the radius of the particles was measured using the dynamic light scattering technique. The final result pointed out that PNiPAM show, as expected a thermo-responsive temperature behaviour which corresponds qualitatively to what is was expected. Moreover another sample of a different colloid, silica nanoparticle, underwent the same process as a control sample, and it was shown that there was no change in radius. Finally the size of the particles concrete size of the particles falls in the expected range, expected from the initial proportions of reagents used in the polymer synthesis. It would have been interesting to compare these results with the theoretical predictions that come from Flory-Rehner theory, which manages to describe this kind of behaviour.

For the glassy phase, our experiment could not attempt to take repeatable measures of the glass dynamics. This occurred, on one side, due to the difficulty to find a good exposure time of the CCD camera to get data which allowed resolving the decay in the correlation of the speckle pattern. But the main difficulty was the aging behaviour of the system, as it turned slower and slower as the time went by. This limited our analysis to not repeatable measures; nevertheless, before the aging behaviour acted in the experiment, we were able to study the relaxation time for different measurements, and it showed a clearly glassy state. This open the doors to new research paths; on one side, it would be possible to use a more dilluted sample to reach en equilibrium state not as slow as the one found in the experiment. On the other side, a quantitatively study in the aging of the system or the research around its causes would be interesting topics to follow on future investigations.

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