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Slow dynamics in dense oil–water emulsions studied using dynamic light scattering

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Abstract

The 3D-echo-DLS (dynamic light scattering) flat cell light scattering instrument (3D-echo-DLS-FCLSI) presents the possibility of measuring slow dynamics of turbid and concentrated colloidal systems. It combines a modified 3D-DLS component and an echo-DLS component with the flat cell light scattering instrument. While the 3D-DLS suppresses multiple scattering, the echo-DLS allows measurements of slow dynamics or even on non-ergodic systems. The advantage of the thin flat cell is that it increases the transmission and reduces multiple scattering; i.e., singly scattered light that is required by the 3D-DLS is still available from dense turbid systems. In the first part of this contribution the 3D-echo-DLS-FCLSI is introduced and the instrumental performance is presented. The second part of the paper is concerned with the ageing behavior of dense fluids in a flat cell, and with confinement effects. Here, we show that ageing is strongly influenced by the process of filling of the flat cell. In some cases complementary methods can be utilized to measure special properties of the system; e.g., the multispeckle method is most appropriate for measuring heterogeneity effects. In the last part of the paper we compare glass transition measurements of an index-matched emulsion carried out using the 3D-echo-DLS-FCLSI and using the multispeckle instrument. We still find an α -relaxation in the glassy state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Dynamic light scattering (DLS) is often used for particle sizing. Along with this standard application there is also a theoretically and experimentally more sophisticated application of this technique: the investigation of the dynamics of interacting colloids. While measurements on the transparent and ergodic systems can be made easily using standard setups, it is still challenging to use this technique for turbid dense systems such as glasses or gels. Two kinds of instrumental methods have been established to date: using cross-correlation echo-DLS and multispeckle diffusing wave spectroscopy (MSDWS) [1–5]. The first method suppresses multiple scattering using the cross-correlation technique [6, 7], and enables an ensemble averaging by the echo method. The second method relies on multiple scattering, using a

diffusion model to describe the propagation of the light across the sample. Additionally, a spatial averaging can be performed to get the ensemble average. Each of the two instrumental methods has advantages and disadvantages. The cross-correlation technique is only effective if enough singly scattered light is transmitted through the cell. Even at low concentrations this is not always the case. On the other hand, MSDWS is only applicable if the light is scattered several times, and the system must be highly turbid to be in this multiple-scattering regime. Furthermore, it does not provide scattering-angle resolution and is not useful for determining polydispersities.

We have recently developed an instrument that uses the 3D cross-correlation technique together with an adjustable thin flat cell [8]. The thin flat cell is useful for reducing multiple scattering and for increasing transmission. We used laboratory-built flat cells where the cell thickness can be varied from 10 μm up to the millimeter range. Additionally, by using crossed polarization filters, we were able to improve

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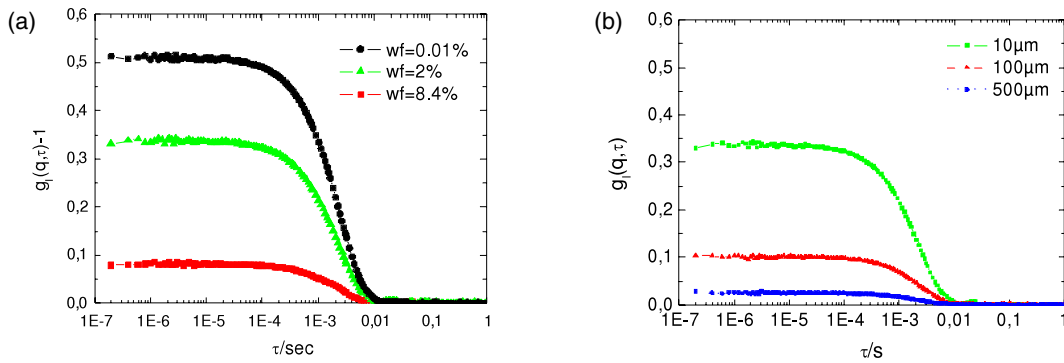


Figure 1. Correlation functions measured with latex dispersion, scattering angle 45° : (a) varying weight fraction wf , cell thickness $10\ \mu\text{m}$. (b) Varying cell thickness at a weight fraction of 2%.

the intercept in the 3D cross-correlation process. In 3D-DLS the intercept is limited theoretically to 0.25; in experiments a typical value of 0.15 is reached. By introducing the crossed polarizers we were able to increase the intercept by a factor of 4 to about 0.6, which represents a greatly improved signal to noise ratio. This new setup reduces the measuring time and allows us to make measurements on more turbid systems than with standard 3D-DLS instruments. Often, turbid systems are concentrated, interacting systems. Measurements on such systems become time-consuming if the dynamics are slow. If the time average is not equal to the ensemble average a standard DLS measurement is not applicable any longer. Such systems are called non-ergodic. A method that dramatically reduces the measurement time and which also allows the study of such non-ergodic systems is the echo-DLS one [1]. The principle of this method is continuous rotation of the sample cell. Consequently, the speckle pattern also rotates, and the correlation function decays quickly because of that rotation, but after every full revolution the speckle comes back to exactly the same position and recovers the dynamics of the sample. These repetitions are called echoes, and they return at multiples of the rotational period. The measurement thus obtained is the average of all the speckles in each revolution. All speckles in a single revolution contribute to the same correlation channel. This produces the final, ensemble-averaged echo. This method can be combined with the cross-correlation technique with some effort. We have developed a mechanical setup that is compatible with our flat cell 3D-DLS instrument, and that provides correlation times of more than 20.000 s.

To learn more about these colloidal systems, we have also installed a multispeckle DLS [9–11]. This provides another important method that gives additional information about the sample, and is in some aspects complementary. In multispeckle DLS, a CCD camera takes a series of pictures of many different speckles at constant time intervals. Each pixel $\text{pix}_{i,j}(t)$ of a frame taken at time t must be correlated with the same pixel $\text{pix}_{i,j}(t + \tau)$ of another frame taken at time $t + \tau$. Averaging over all the pairs of correlated pixels $\langle \text{pix}_{i,j}(t)\text{pix}_{i,j}(t + \tau) \rangle$ leads to a good approximation for the ensemble-averaged correlation function at τ . By correlating each picture with all the other pictures taken at times $t + n\tau$ ($n = 1, 2, 3, \dots$) a complete correlation curve is obtained. This method is

as fast as using echo-DLS; i.e., the measurement time is equal to the longest correlation time. Because the sample does not need to be moved there is no danger of disturbing it. However, multispeckle DLS cannot be combined with the cross-correlation technique for the suppression of multiple scattering, which can only be partly reduced [12]. The method can therefore not be applied to highly turbid systems.

By comparing the results from the two instruments we can monitor the mechanics of our echo-DLS setup. A further advantage of the multispeckle technique is that it provides the opportunity to measure time-resolved correlations. In this way the sample heterogeneity and temperature fluctuations can be monitored. A disadvantage is the poor angular resolution, which makes measurements at q -positions with strong changes in $S(q)$ difficult or even impossible.

In this paper we present further properties of the 3D-echo-DLS flat cell instrument (3D-echo-FCLSI) that were not mentioned so far. The ageing behavior in the flat cell used here is discussed afterward. This is the first application of this instrument and could be of general interest. The following phase transition measurements show the kinds of results we could get at very long correlation times. Some of the measurements were made prior to the installment of the 3D-DLS component. Consequently, most of the samples were index matched. This also facilitated comparison with the multispeckle instrument.

2. The 3D-echo-DLS flat cell instrument

2.1. The modified 3D-DLS setup

The instrument was placed in the vertical direction to allow for horizontal rotation of the sample cell. $\lambda/4$ plates and polarization filters were installed to decouple DLS experiments 1 and 2 which are cross-correlated. The theoretical intercept should be 1 instead of 0.25. We could reach typical intercepts between 0.5 and 0.75; details of the setup can be found in [8].

Figure 1(a) shows a concentration series measured using the 3D-echo-DLS-FCLSI with standard latex spheres of a hydrodynamic radius of 113 nm. The scattering angle was 45° and the cell thickness $10\ \mu\text{m}$. It can clearly be seen that the intercept decreases with increasing weight fraction, which is due to the increasing amount of multiply scattered light. The

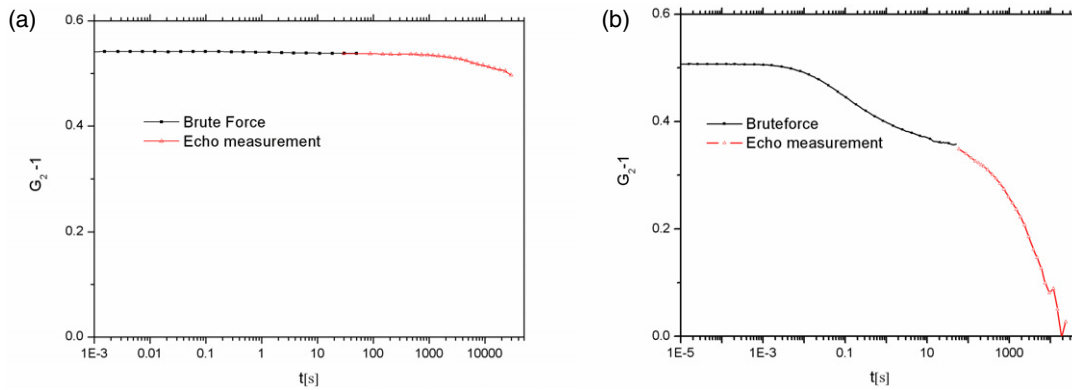


Figure 2. Measurement with the 3D-echo-DLS-FCLSI with non-index-matched emulsions. The particle diameter was 1400 nm, the scattering angle 17° . (a) Cell thickness $10\ \mu\text{m}$, weight fraction 75.7%. (b) Cell thickness $10\ \mu\text{m}$, weight fraction 60%.

weight fraction of the dispersion delivered by the producer was $wf = 8.4\%$. The results indicate that samples with even higher wf values could be measured. The influence of multiple scattering increases with cell thickness. At $wf = 2\%$ and a scattering angle of 45° the use of a $100\ \mu\text{m}$ cell instead of a $10\ \mu\text{m}$ cell reduces the intercept by a factor of around 3 (see figure 1(b)).

2.2. Echo-DLS

We have examined the echo-DLS instrument in three ways: a ground-glass test, which shows a constant correlation function; a test with latex spheres in glycerol that shows a predictable relaxation; and a comparison between multispeckle DLS and echo-DLS, which tests whether vibrations disturb the echo measurements. All these tests were successful [8]. The maximum measurement time is limited by the mechanical properties of the instrument (gears, motor, bearing, and controller). While the short time-speed fluctuations, which cause a smearing of the echoes, can be corrected by an area correction, the long-term drift of the speed terminates the measurement.

2.3. 3D-echo-DLS flat cell instrument

Figure 2(a) shows the initial measurements with this instrument. The sample is a non-index emulsion. The particle weight fraction was 75.7% and the particle diameter $1400\ \mu\text{m}$. For this measurement we used a cell thickness of $10\ \mu\text{m}$. The scattering angle θ was 17° . The intercept was 0.54. In figure 2(b) a $10\ \mu\text{m}$ cell was again used, but here the particle weight fraction of a similar non-index-matched emulsion was only 60%. We still reach an intercept of 0.51 at $\theta = 17^\circ$. By increasing θ the intercept could be further improved because multiple scattering is orientated in the forward direction.

3. Ageing behavior in the flat cell

When we filled the cell we deposited a drop of the sample in the middle of the glass window of one half of the cell. The cell was then closed by placing the two halves together. The sample was squeezed towards the outer rim and finally filled



Figure 3. The two accessible measuring positions are marked in white.

the closed cell completely. In the following example we used a non-index-matched oil-in-water emulsion (Siliconoil DC200, $d = 0.968\ \text{g ml}^{-1}$, surfactant Triton X 100) with a droplet diameter of 760 nm and a cell thickness of $10\ \mu\text{m}$.

With echo-DLS we have measured the dynamics at different sample ages t_{age} at two different positions in the cell. In the cell center we are able to measure at a fixed position. In the outer position we measure on a concentric circle, averaging over all dynamics on this circle (see figure 3). In the inner part of the cell, which is the visible part of glass plates with 20 mm diameter, we find almost frozen dynamics directly after filling the cell.

The outer part of the cell, where the glass plates are glued to the frame, is not accessible. This part has a width of 5 mm. In both accessible measuring positions we found a high plateau without ageing ($t_{\text{age}} = 0\ \text{d}$), meaning the particles can hardly even ‘rattle in their cages’ (see figure 4(a)). This would correspond to an almost close-packed density. On the other hand, for such high concentrations an α -decay is not expected, but it is found in our system, which might indicate that the sample is heterogeneous.

For 6 h the sample relaxed, i.e. the particles recovered space to move in their cages. But the different decays measured at the different positions show that the sample was still not homogeneous. Only after three days was the dynamics homogeneous throughout the cell.

The main ageing process, however, was not completed for 7–11 d. During this ageing the α -decay shifts to higher timescales [13–16]. This ageing already starts during the

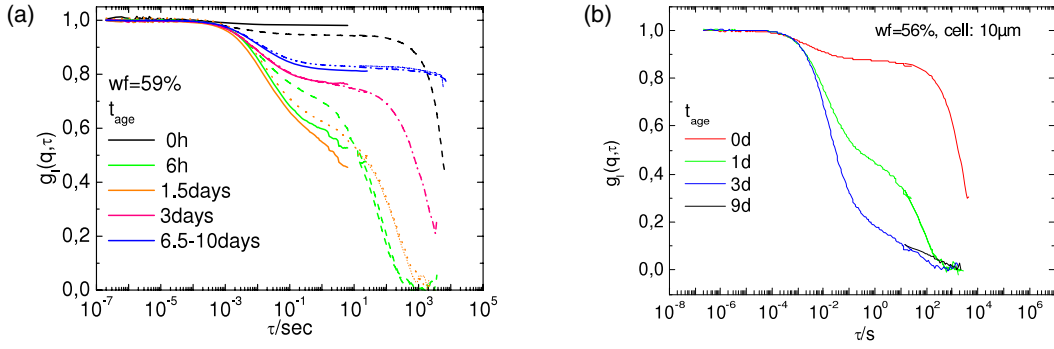


Figure 4. (a) Ageing of densely packed emulsions (volume fraction $\Phi \approx 60\%$): correlation functions taken in the center (dotted lines) and at the outer boundary (solid lines) of the cell at different ageing times. (b) Correlation functions at $\Phi \approx 57\%$ taken in the cell center.

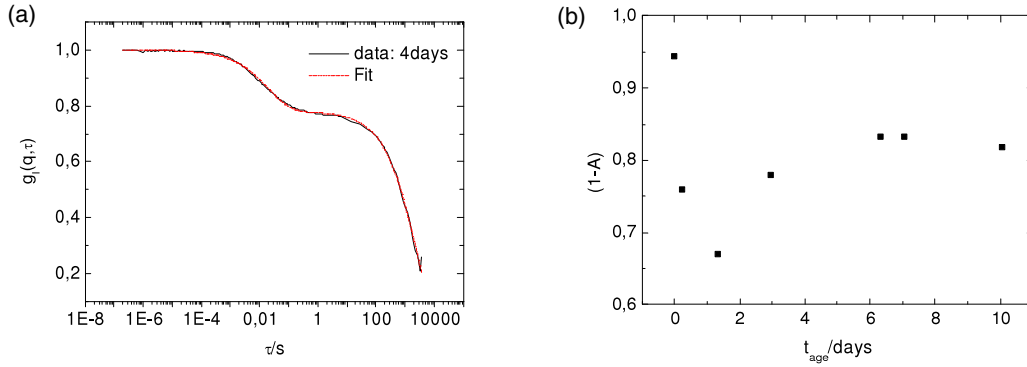


Figure 5. (a) Result of the fit. (b) Dependence of the plateau height $1 - A$ as a function of ageing time t_{age} .

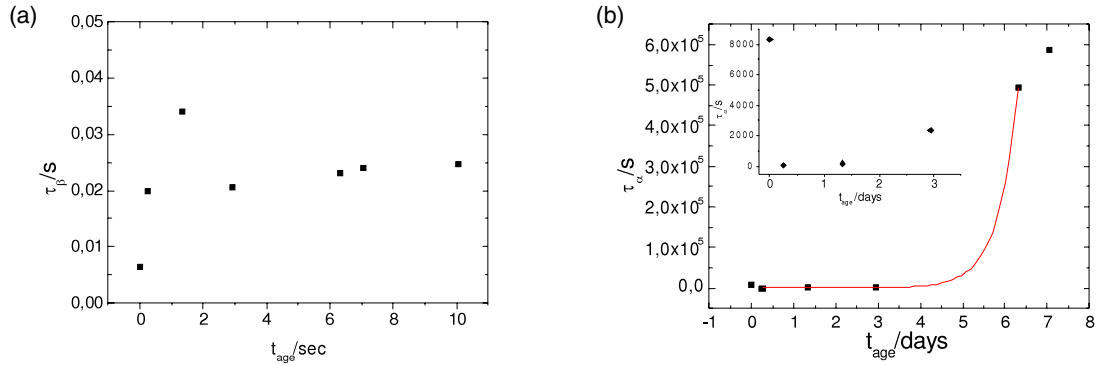


Figure 6. The sample ageing time (t_{age}) dependence for both relaxation times τ_β and τ_α . (a) The β -relaxation time τ_β shows a peak at $t_{\text{age}} < 3$ d. (b) The α -relaxation time τ_α shows a strong decrease over the first hours, a minimum after 6 h, and later exponential growth. The inset documents the changes at $t_{\text{age}} \leq 3$ d. The solid line is an exponential fit between $6 \text{ h} < t_{\text{age}} < 6.5$ d.

first and the second day, while, at the same time, the plateau height still decreases. This is an unusual behavior, most probably caused by sample homogenization due to solvent back-diffusion.

In a more quantitative evaluation (at the center position) of the data in figure 4(a) we have fitted the β -decay and α -decay with

$$g_2(q, t) - 1 = Ae^{-\left(\frac{t}{\tau_\beta}\right)^\beta} + (1 - A)e^{-\left(\frac{t}{\tau_\alpha}\right)^\alpha}. \quad (1)$$

This formula considers stretched exponentials for both decays. In figure 5(a) the fit result is shown. $1 - A$ is a good

approximation of the plateau height, which shows a minimum at $t_{\text{age}} = 2$ d and stays constant after 6.5 days (figure 5(b)).

The β -decay, described by τ_β , is time dependent for $t_{\text{age}} \geq 3$ d (see figure 6(a)), but shows a minimum at $t_{\text{age}} = 0$ d and a maximum at the timescales where the short time dynamics relaxes back.

The α -decay, τ_α , shows first a decrease and then a moderate increase (see also the inset in figure 6(b)). Between 3 and 6.5 d the shift to higher timescales becomes enormous. The development of τ_2 with sample age t_{age} cannot be described using a power law in this time regime (of the kind $\tau_2 \sim$

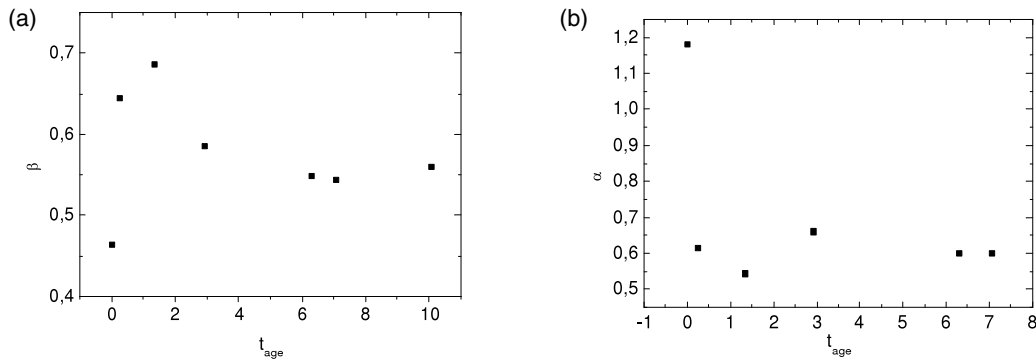


Figure 7. The dependence of the stretching parameters α and β on t_{age} . (a) β shows a peak during the first three days. (b) α drops from a value above 1 to being almost constant at 0.6.

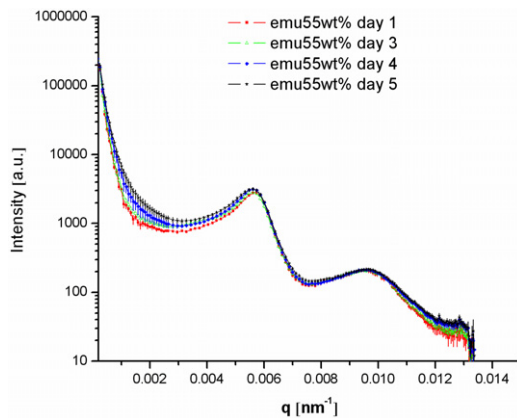


Figure 8. Static light scattering curves of an emulsion with 55 wt% recorded at the rim of the sample cell over a time of five days.

t_{age}^{μ} [13, 17, 18]) but requires an exponential law [19, 20], of the type $\tau_{\alpha} = \text{const} + e^{t_{\text{age}}/\mu_{\text{exp}}}$ with $\mu_{\text{exp}} = 41\,600$ s.

The β -exponent shows a peak similar to that of τ_{β} (see figure 7(a)). The α -exponent falls from 1.2 at $t_{\text{age}} = 0$ d to around 0.6 for $t_{\text{age}} > 0$ d. Because the α -decay was not measured completely at $t_{\text{age}} = 6.5$ and 7 d, neither the α -exponent nor τ_{α} could be determined precisely (the fit would also allow higher values for τ_{α} if α were not limited to $\alpha \geq 0.6$).

This ageing behavior was investigated at a volume fraction of around 60% (see figure 4(a)). At a smaller volume fraction (figure 4(b)), the starting behavior is quite similar. Also here the dynamics are strongly frozen at $t_{\text{age}} = 0$ d. Over subsequent days the dynamics became faster. After three days the correlation function is stabilized. No further ageing occurs.

If we assume that the solvent moves during cell closing with a higher velocity than the particles, it is possible that a concentration gradient occurs that leads to frozen dynamics in the cell. The dynamical change measured in the first three days would then be caused by the back-flow of the solvent. In the literature such dynamical behavior in flat cells has not been mentioned so far, i.e. it is possible that the filling process and cell geometry can have an influence on the dynamics measured. Methodical differences can also lead to different observations, e.g. confocal microscopy studies on confined gels or glasses

detect smaller measurement volumes than echo-DLS ones. The timescales on which the dynamics were measured could also be different. For example, in a comparable work of Eric Weeks [21] on glass transitions observed in confinement he mentioned a scanning time of his confocal microscope of 1 h. But it is not reported whether the measurement was repeated on the following days and how long the waiting time after filling of the cell was.

We used static light scattering to examine the structural change during the ageing process (see figure 8). The sample was an index-matched emulsion with 48% glycerol. The droplet size was 1400 nm, and the cell thickness 10 μm . The structure was almost constant at all positions and all times. This challenges the assumption that there is a concentration change in the first ageing period. However, numerical simulation of $I(q)$ shows that this static scattering function does not change considerably between 55% and 70%.

4. Concentration series of an oil-in-water emulsion

A glass transition is theoretically predicted for colloidal systems at a volume fraction of 58% and has also been experimentally found in several systems [22–27]. The transition is characterized by the divergence of the α -decay time τ_{α} ; i.e., the system becomes non-ergodic. We wanted to investigate whether such an ergodic-to-non-ergodic transition, or glass transition, can also be found in dense emulsions. For this measurement series we used a cell thickness of 500 μm to avoid confinement effects, which can lead to a linear final decay [28, 29]. One such example is shown in figure 4(b) (10 μm cell, $t_{\text{age}} \geq 3$ d). Another example is shown in figure 9. The measurements were performed with index-matched emulsions (emulsions similar to those mentioned above with a droplet diameter of 1040 nm, where 48% glycerol was used for index matching) with a weight fraction of 57% in a 100 μm and in a 500 μm cell.

While the result for the 500 μm cell shows the expected exponential decay, the same sample measurement for the 100 μm cell shows a linear decay. Because ageing was not complete the second measurement was made immediately after the first, omitting the time-consuming brute force measurements.

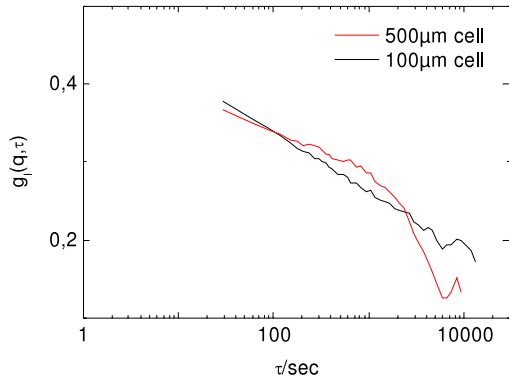


Figure 9. α -decay in a 100 μm and in a 500 μm cell. The sample is an index-matched emulsion ($wf = 57\%$) with the same ageing time.

The statistical errors of the last few data points of each curve are higher because of the less effective averaging. The experimental settings were the same in the two cases. The scattering angle was $\Theta = 21.2^\circ$. Heterodyning was not seen at this angle in reference measurements [8]. As the index was not totally matched, the sample still scattered strongly enough that heterodyning could be neglected.

The following concentration series was measured with emulsions similar to those mentioned above, having a mean diameter of 1040 nm. We used 40% DMSO in water to index match the sample. In this series we have increased the volume fraction Φ from 58% to 62%. The plateau height increases, as expected, with the volume fraction (see figure 10). In addition,

the plateau height follows the height of the structure factor (see figure 10, lower right).

This finding is typical for a repulsive system [22]. However, at all concentrations we found a second relaxation (α -relaxation), indicating that the system remains ergodic. This phenomenon has been previously observed by Gang *et al* [30], who reported that oil droplets can be deformed, whereby the α -relaxation will be enabled also in the glassy state.

From our results we conclude that heterogeneity or temperature instabilities could also explain the findings. Unfortunately, echo-DLS can only be used to measure a time-averaged correlation. Therefore, we used the multispeckle method to resolve the temporal changes of the dynamics. Fluctuations on higher τ -channels occur (see figure 11), that could be provoked by slow explorations of different dynamical states, characterized by widely different mobilities [31].

On the other hand, temperature fluctuations on this timescale could also induce such changes [32]. The temperature stabilization of our multispeckle instrument was not better than 0.1°C , so heterogeneity as well as temperature fluctuations could be the reasons for the changes at this stage. For both effects, independence of q would be expected for the α -relaxation.

The linear increase of the α -decay with the volume fraction is not profound. Here it must also be considered that the α -relaxation is not completely reproducible but varies slightly because of the fluctuations at higher τ -channels (see figure 12(a)).

The multispeckle measurements were performed only at $q = 5 \mu\text{m}^{-1}$ (figure 12(b)). At this angle the structure factor is

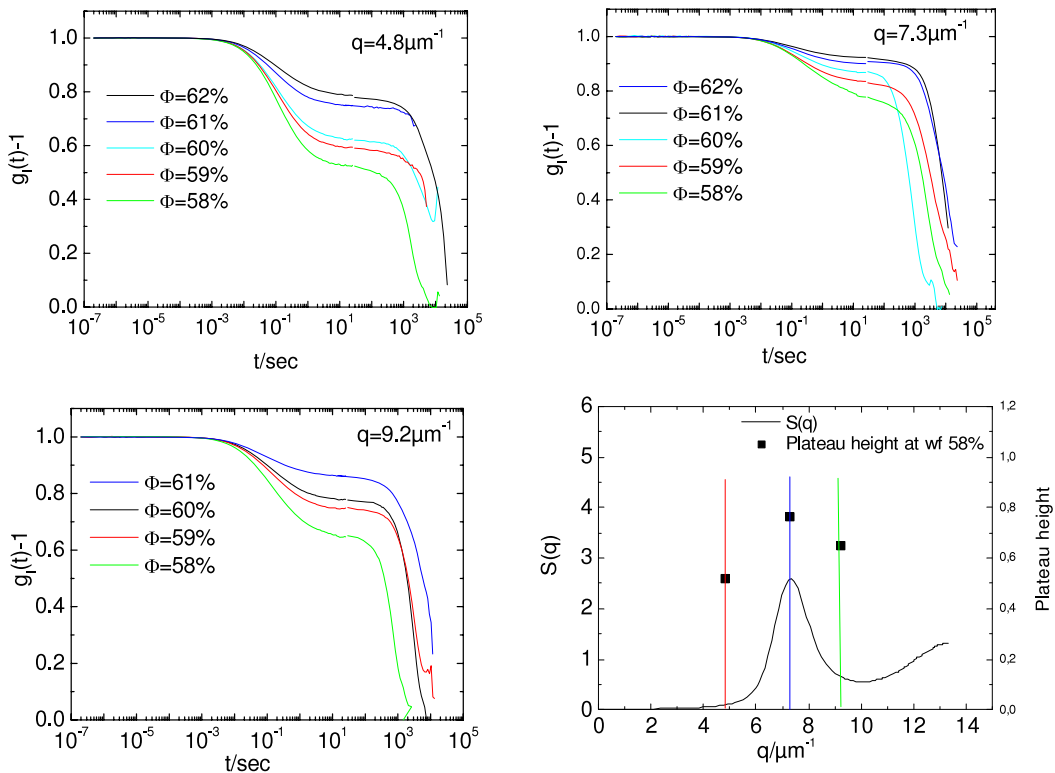


Figure 10. Correlation functions at several volume fractions ($\Phi = 58\%$ – 62%). The sample used was an index-matched emulsion in a 500 μm cell. Lower right: the static structure factor of the index-matched emulsion used. The vertical lines are the measurement positions for the correlation functions, while the squares represent the plateau heights at these q -vectors.

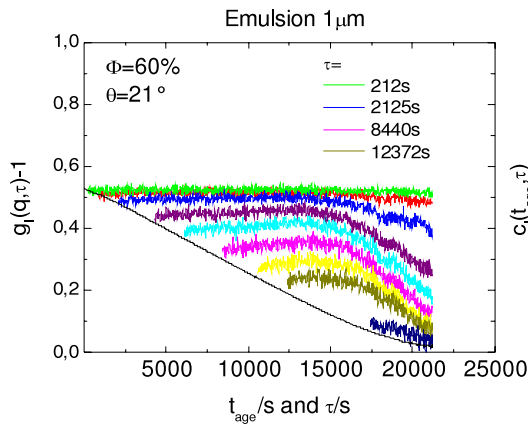


Figure 11. Intensity correlation function $g_1(q, \tau) - 1$ and time-resolved correlation functions $c_1(t_{\text{age}}, \tau)$ at different τ -channels measured by the multispeckle instrument. The sample is the same index-matched emulsion as was used in the echo-DLS experiments shown in figure 10.

quite flat. The time-averaged correlations of the multispeckle experiment and the echo-DLS curves are in good agreement at this scattering angle.

5. Conclusions

We have used the recently developed 3D flat cell instrument to make measurements on turbid and non-ergodic colloidal systems. A first result is that the ageing behavior in thin flat cells is different from usual behavior in wider cuvettes. The procedure of filling of the flat cell strongly disturbs the sample. The shearing that occurs during cell closing may cause a concentration gradient: the solvent (here water) was squeezed to the cell boundary while the particles mainly remain in the center of the cell. Consequently, at $t_{\text{age}} = 0$ d the sample is strongly frozen in the accessible range of the cell. Then, as t_{age} increases, the ageing is superimposed by the back-flow of the solvent, which causes strong changes in the relaxation times (α - and β -decay) and in the plateau height.

The increase in the α -relaxation time (starting at $t_{\text{age}} \approx 1.5$ days) with sample age does not follow a power law in the time interval $6 \text{ h} < t_{\text{age}} < 6.5$ days, but shows an exponential

behavior. A possible explanation for this faster ageing is that the system is further away from equilibrium at the beginning of the measurement.

Then we studied a concentration series of emulsions where we used a thicker ($500 \mu\text{m}$) cell to avoid confinement effects. Here the oil-in-water emulsions were index matched with DMSO in order to facilitate comparison with the multispeckle measurements. At all concentrations a second relaxation was found, showing that the samples remain ergodic. Furthermore, at correlation times $\tau > 10^4$ s the curves showed an instability, changing its functional form during the measurements.

We therefore repeated the measurements with the multispeckle instrument, and found strong fluctuations in the higher τ -channels, which are the cause of the unstable curve progression in the echo-DLS measurements. Either heterogeneities or temperature instabilities could explain these fluctuations, which in turn may give rise to the scattering-angle independence of the α -decay and its small concentration dependence. The ageing measurements discussed above were not visibly affected by these fluctuations because of the short relaxation times.

In future we plan to improve the temperature stabilization of our instrument and to investigate various turbid systems of practical interest such as gelling emulsions.

Acknowledgments

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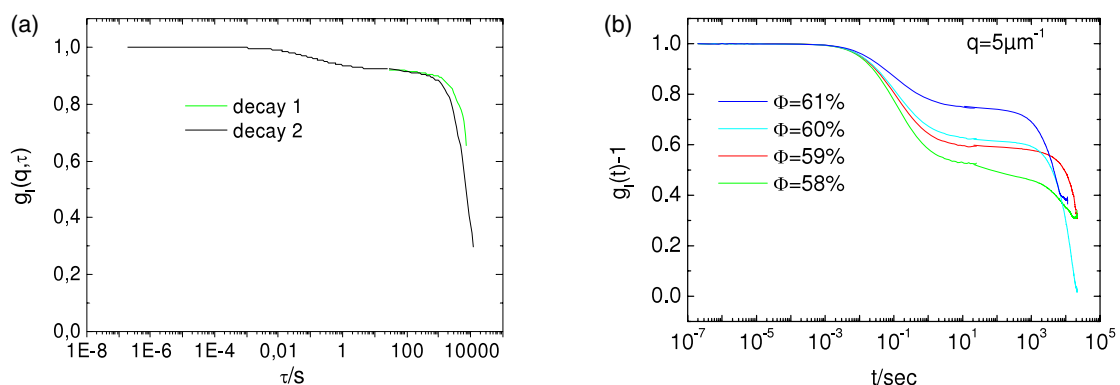


Figure 12. (a) Correlation function measured using echo-DLS. The repetition of the α -decay measurement shows a variation in the decay time ($\Phi = 61\%$, $q = 7.33 \mu\text{m}^{-1}$). (b) Concentration series measured with the multispeckle instrument. Here the scattering vector is $5 \mu\text{m}^{-1}$. The sample belongs to the same series as the echo-DLS measurements were made on (index-matched emulsion).

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