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A look inside particle stabilized foams particle structure and dynamics

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Abstract

From a physico-chemical point of view, most food is soft matter. Usually, these systems are complex in the sense that they combine multiple ingredients with a wide range of structural length scales and dynamics on various time scales. Amongst these systems, foams belong to the well studied but less well understood systems. Particle stabilized foams are very common in food systems. As a model system, we produced aqueous foams from silica nanoparticle dispersions. The silica nanoparticles were hydrophobized by the *in situ* adsorption of shortchain alkyl amines of chain length C_5 to C_8 to render them surface active. We determined the role of the particles in stabilizing the produced foams. It is shown that the depletion of the bulk silica concentration during the foam formation can be quantified by precise density measurements. In the case of nanoparticle aggregation, more particles are trapped in the foam and will form a network in the foam channels. Diffusing wave spectroscopy was used to study the different time and length scales of the composite system. We find that it is possible to obtain the size of the particles within the foam by two different approaches. Additionally, the dynamics of the foam network is analyzed and it is confirmed that the formation of an aggregated particle network within the foam is responsible for a deceleration of the foam structure evolution.

Keywords: foams, diffusing wave spectroscopy, nanoparticles, dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction

Most of what we eat is soft matter [1]. Usually, food systems are composed of a vast number of ingredients and often, the samples are not transparent. Thereby, these systems are not conveniently accessible for most optical techniques.

For systems with a high degree of multiple scattering, diffusing wave spectroscopy (DWS) is a useful tool for investigating the dynamics and structures at different time and length scales. The theory can be regarded as well elaborated [2–7] and has been applied in various fields of research, especially in the soft matter community [8, 9] and food science [10–12]. Examples of systems whose parameters have become optically accessible by the use of DWS are highly scattering dispersions [13, 14], emulsions [15–17] and foams [18].

The technique enables one to probe the diffusion processes of the constituents in the sample by optical means. Therefore, contactless microrheological measurements can be performed [19–21]. Changes in particle size and network formations can be detected [22, 23]. Both approaches are used in the research of food colloid systems. In the industry, mouth-feel and flow properties are very important in food product design [24]. Hence, it is desirable to obtain information about the correlation of microstructure and the sensory aspect of a food product. Milk is one of the most investigated systems [25, 26], especially its response to changes in the environment (pH, temperature, ionic strength) e.g. in the process of cheese making [27, 28]. The temporal evolution of emulsified systems is another topic of interest that can be covered by DWS [29]. Reviews of food systems studied by DWS can be found in the literature [30, 31].

As an example of highly light scattering soft matter, foams are suitable candidates to be studied by DWS [32–36]. Durian *et al* extensively used diffusing wave spectroscopy to study the

temporal and structural features of classical surfactant foams [18, 37, 38]. From the culinary point of view, foams can be found as e.g. a molecular-kitchen-style gelled foam [39], coffee crema, whipped cream, beer heads or milk-foams [40]. Many of the food foams are stabilized by proteins or aggregates of proteins. These can be regarded as particle stabilized foams with proteins playing the role of the surface active ingredient.

In this kind of system, a fraction of the present particles is used to stabilize the liquid/air interface. A large fraction of particles remains in the bulk phase that is held up in the foam structure (plateau borders, vertices) [41, 42]. Similar model systems have recently been investigated using hydrophobic aggregates of silica particles [43, 44]. These systems possess features at different time and length scales. The nanoparticles are very small compared to the large bubbles of the foam. Likewise, the particle motion is orders of magnitude faster than the dynamics of the foam structure [34, 36].

As a model system for particle stabilized foams, we use foams created from silica nanoparticle dispersions. The nanoparticles are rendered hydrophobic by the *in situ* adsorption of short-chain alkyl amines of chain length C_5 to C_8 . Solutions of the aliphatic amines themselves do not show any noticeable foamability, in contrast to long-chain surfactants. Crassous and Saint-Jalmes proposed a theoretical framework [36] to analyze DWS data obtained from systems of mixed scatterers like nanoparticles and foam bubbles. We will show that this model can be used to explain the experimental results of our nanoparticle stabilized foams. It is shown that the particle and foam dynamics are well separated. The particle sizes can be determined in the foam with two different approaches with satisfactory agreement. Additionally we will clarify the increased stabilization of the foams found when particle aggregation occurs.

2. Experimental section

Stock solutions of the amines were prepared and adjusted to pH 10.3 via the addition of 1M HCl. The stock concentrations were 0.5 M for pentyl amine and hexyl amine, 0.05 M for heptyl amine and 0.02 M for octyl amine. For the longer chain amines (C_6 to C_8), a clear solution was obtained when adjusting to the final pH. A silica stock solution of 50 g L⁻¹ Ludox TMA containing 0.1 mol L⁻¹ methyl amine was prepared. The methyl amine was used as a buffer to keep the pH of the dispersion constant. A 1M methyl amine solution was added dropwise to a silica dispersion which was previously diluted with ultrapure water. During the preparation, the pH was monitored. Small amounts of 1M HCl were added dropwise, when needed, to ensure that the pH did not increase above 10.5. The final volume was adjusted in a volumetric flask. The final adjustment of the volume did not affect the pH.

To prepare the samples, the amine stock solutions were diluted to twice the desired final sample concentration and then mixed 1 : 1 with the silica dispersion to achieve the desired amine concentration and a silica concentration of 5, 25 g L^{-1} or 50 g L^{-1} and a methyl amine concentration of 0.05 M. Mixing was done on a vortex mixer which avoided excessive foam production during the sample preparation.

2.1. Dynamic light scattering (DLS)

Samples of silica concentration $5 \text{ g } \text{ L}^{-1}$ were used to study the concentration dependent aggregation behavior. The samples were prepared and left to age undisturbed for three days. Dynamic light scattering data were recorded using an ALV/ CGS-3 compact goniometer system equipped with an ALV-7004/USB correlator. Temperature control was provided by a Huber Compatible Control thermostat. The laser wavelength was 632.8 nm, and the laser light was polarized perpendicularly to the scattering plane. Intensity autocorrelation functions $g_2(\tau)$ were recorded at a scattering angle of 90°. The Siegert relation was used to calculate the field autocorrelation function $g_{l}(\tau)$. Second order cumulant analysis was used to extract the relaxation rates Γ of the autocorrelation functions. With known Γ and scattering vector q, the particle diffusion coefficient D is calculated by $D = \Gamma/q^2$. Applying the Stokes–Einstein equation yields the apparent hydrodynamic particle radius $R_{\rm h}$

$$R_{\rm h} = \frac{k_{\rm B}T}{6\pi\eta D} \tag{1}$$

with the thermal energy kT and the dynamic dispersion viscosity η .

2.2. Particle extraction and foam volume

In order to quantify the amount of particles in the bulk dispersion, density measurements were performed with an Anton Paar DMA 4100 density meter. Bulk density measurements of silica dispersion samples with known mass concentration β revealed a perfectly linear dependence of bulk density on the mass concentration of particles. Sample volumes of 6 mL were used for the extraction experiments. The silica mass concentration was 25 g L^{-1} for all experiments. Gentle vortex mixing was crucial to avoid foam formation during the mixing process. Subsequently, 3 mL of the prepared sample dispersion were separated and the dispersion bulk density was measured. The remaining 3 mL of the sample in the test vial were vigorously shaken by hand for 40 s. Immediately after foaming, the produced foam volume was measured with the help of the graduation on the vial. As the foam drained, 1.5 mL of the dispersion was sampled from the bottom of the vial with a syringe and needle. Again, the bulk density was measured. The reference measurements with known mass concentrations were used to determine the silica mass concentration β of the unfoamed and foamed dispersion. Calculating the extracted fraction α of particles was straightforward

$$\alpha = \frac{\beta_{\text{unfoamed}} - \beta_{\text{foamed}}}{\beta_{\text{unfoamed}}}.$$
(2)

2.3. Diffusing wave spectroscopy (DWS)

For the experiments, 4 mL of sample dispersion with a silica mass concentration of 50 g L^{-1} were whipped for 60 s with a hand-held milk frothing device. Afterwards, the sample was quickly transferred to the sample cell. A flat cell of width 5 mm was used. The cell was 50 mm wide in order to ensure no light escaped through the sides. Only samples with long enough



Figure 1. Hydrodynamic radius of the nanoparticles as a function of amine concentration. For all amine carbon chain lengths, aggregation is visible above the critical amine concentration (CAC). Silica concentration 5 g L^{-1} .

foam life-times and proper handling properties (stiffness) could be assessed. The sample cell was weighed after the sample was inserted which allowed us to calculate the mean liquid fraction Φ_l of the foam. Diffusing wave spectroscopy measurements were performed using an ALV goniometer system equipped with an ALV/LSE-5004 correlator. Temperature control was provided by a Huber Compatible Control thermostat. The incident laser beam (Nd-YAG, 532nm) was expanded to illuminate an area of approx. 4 cm². All measurements were performed in transmission geometry. Apertures were used to collect scattered light from an area roughly corresponding to a speckle. A photomultiplier tube connected to the autocorrelator yielded the normalized intensity autocorrelation function $g_2(\tau)$. Consecutive measurements of 120 s were performed until either the foam collapsed or a maximum time of 30 min was reached. Data analysis is heavily based on the model presented by Crassous and Saint-Jalmes. All samples were freshly prepared and measured three times. The samples were measured within the first 10 min after preparation. As the transmission increased more than 30% from the starting value, the data were not used for further analysis.

3. Results

The bulk behavior of the particle dispersions was assessed by DLS measurements. The particle radius was determined as a function of the amine concentration. As can be seen from figure 1, the particle radii remain nearly constant up to a



Figure 2. Fraction of particles that are immobilized in the produced foam, as a function of amine concentration and chain length. Above the CAC, a lot of particles are trapped in the foam due to aggregation and gel formation in the foam matrix. Silica concentration 25 g L^{-1} .

concentration at which aggregation starts. This concentration will be referred to as the critical amine concentration (CAC). The volume fraction of silica used in these measurements was chosen to be 0.005. Above the CAC, at higher silica volume fractions of 0.05, strong aggregation occurs and the samples form a gel within hours.

The particle extraction experiments clearly show that the foaming process depletes the bulk phase of silica particles as measured in the drained liquid. In figure 2, the fraction of extracted particles α is plotted as a function of the amine concentration. Approximately linear dependencies are found for the amount of particle depletion and the logarithm of amine concentration. Particle dispersions without additional amines show no foamability. As expected, no foam formation goes along with no change in the particle concentration before and after shaking. Above the CAC, the amount of particles in the drained liquid is strongly decreased compared to the amounts below the CAC. This means that more particles are trapped in the foam above the CAC.

Figure 3 shows the dependence of the produced foam volume on the extracted particle fraction α . A roughly linear dependence is found for low values of α . When large amounts of particles are extracted, the foam volume decreases, this is again coincident with the aggregation of silica particles. Above the CAC, the produced foam volume is strongly reduced compared to the foam volume close to the CAC.

The DWS autocorrelation functions show two temporally separated decays/decorrelations as depicted in a lin–log representation in figure 4(a). The decorrelation is caused by the



Figure 3. Produced foam volume as a function of extracted particle fraction. The linear dependence indicates an approximately constant number of particles per air bubble. Silica concentration 25 g L^{-1} .



Figure 4. (a) lin–log plot of the field autocorrelation function $g_{\rm I}(\tau)$ of the transmitted light intensity. (b) log–lin plot of $g_{\rm I}(\tau)$ with an exponential fit to extract the characteristic rearrangement time of the foam. (c) Field autocorrelation function $g_{\rm E}^{B}(\tau)$ as calculated by (3) with the corresponding fit to obtain the particle diffusion time. Silica concentration 50 g L⁻¹.



Figure 5. Brownian diffusion time of the particles as a function of amine concentration and chain length. An increase can be seen above the CAC which indicates aggregates. Silica concentration 50 g L^{-1} .

dynamics of the scatterers and the matrix. Experiments on foams with and without additional dispersed particles have shown that the first (fast) decorrelation at small lag times τ is caused by particles diffusing within the foam matrix [34]. The second (slow) decorrelation at larger lag times is caused by pronounced dynamics of the foam matrix itself. In figure 4(b), the data are plotted on a log–lin scale. It can be seen that the second decorrelation is approximately exponential. The corresponding data region can be fitted by a single exponential function $g_{\rm E}(\tau) = g_{\rm E}^* \exp(-\tau/\tau_0)$ leading to a respective decay time τ_0 that is a measure for the dynamics of the foam matrix. Additionally, the amplitude $g_{\rm E}^*$ is a measure for the magnitude of the first decorrelation. Surprisingly, the first decorrelation was almost absent for samples above the CAC.

The following data treatment is heavily based on the approach demonstrated by Crassous and Saint-Jalmes [36]. For a detailed derivation of the theory and the corresponding formulas, the reader may refer to the original paper. The authors have shown that the first decorrelation signal can be separated from the second decorrelation signal, leading to a field autocorrelation function $g_{\rm E}^{(B)}$ that solely depends on the signal caused by the particle movements. That signal $g_{\rm E}^{(B)}$ is calculated from the measured autocorrelation function $g_{\rm E}^{(\pi)}$ and the fit values of τ_0 and $g_{\rm E}^*$ through

$$g_{\rm E}^{(B)}(\tau) = -\frac{\ln \frac{g_{\rm E}(\tau)}{g_{\rm E}^* \exp(-\tau/\tau_0)}}{\ln(g_{\rm E}^*)}.$$
(3)



Figure 6. Foam rearrangement times as a function of amine concentration and chain length. Larger times reflect slower dynamics of the foam matrix, namely bubble rearrangements and film ruptures. Silica concentration 50 g L^{-1} .

An example is shown in figure 4(c). This calculated signal can be fitted to extract a decay time $\tau_{\rm B}$ that is representative for the motion of the particles in the foam. The fit function used is

$$g_{\rm E}^{(B)}(\tau) = \left[1 - \exp\left(-\frac{\tau}{\tau_{\rm B}}\right)\right] \frac{\tau_{\rm B}}{\tau}.$$
 (4)

Figure 5 summarizes the Brownian decay times τ_B as a function of the amine concentration and chain length. The dominant decay time is ≈ 0.23 ms for all the samples studied. This decay time is almost independent of the amine concentration until the CAC where a slight increase is visible. One should keep in mind that the $g_E^{(B)}(\tau)$ signal became comparatively noisy above the CAC. For further analysis, it is necessary to perform further calculations regarding the slow decay times τ_0 which are caused by the foam dynamics. In order to gain comparable information about the foam, we have to calculate the rearrangement time τ_R which is a measure for how fast the foam structure changes per unit time. Larger values reflect a slower evolution of the foam structures. It can be calculated from τ_0 as follows

$$\tau_{\rm R} = \frac{\tau_0 L^2}{2(l^*)^2} \tag{5}$$

with the sample width L and the transport mean free path length l^* . The transport mean free path length l^* can be calculated from the transmitted intensity I of the sample. With a reference sample of known l_{ref}^* , the sample l^* is calculated by $l^* = (I/I_{ref}) \cdot l_{ref}^*$. We used latex particle dispersions of



Figure 7. Logarithm of plateau value g^* between the two decays of the autocorrelation function $g_1(\tau)$ as a function particle volume fraction. The linear relation can be fitted to yield a measure of the particle size. Silica concentration 50 g L⁻¹.

known particle size and concentration as the reference. The l^* value of these dispersions is calculated by Mie theory and their transmitted intensity l_{ref}^* is measured. In figure 6, the rearrangement times τ_R are shown as a function of the amine concentration and chain length. The values are averages over the total measurement time for every sample. With increasing amine concentration, the rearrangement time increases and reaches its maximum value at the CAC. This behavior is seen for all amine chain lengths.

Theory predicts a linear dependence of the logarithm of the plateau values g_E^* on the particle volume fraction (*in the foam*). That is, considering the apparent dilution of the bulk particle concentration due to the presence of air bubbles. Since the DWS samples were weighed, the mean liquid fraction Φ_l is known at least at the start of each experiment. The silica particle mass concentration in bulk (no foam) is also known. Depletion effects which were discussed previously are ignored due to their low impact on the bulk particle concentration. With known particle density, the particle fraction Φ_p in the foam can therefore be calculated.

The theoretical linear dependence is confirmed in figure 7. Samples above the CAC, where particle aggregation is likely to occur, were not included in the analysis. When aggregation was visible in the sample, the first decorrelation was absent in most cases, as stated above.

Linear fits of the slopes for each amine chain length are summarized in the following table. The mean value of l_0^* for the corresponding samples is included for further analysis. Here, l_0^* represents the mean of the transport mean free path length of the foam within the first 5 min

of the experiment. During this time, no substantial coarsening was observed.

C_n	Slope	l_0^* (μ m)
C ₅	78±6	191±57
C ₆	86±5	209±68
C ₇	107±6	174±22
C_8	111±8	154±34

4. Discussion

It is clear from the results that the aggregation of the particles at the CAC has a pronounced influence on the structure and dynamics of the foam matrix. We will discuss the bulk behavior of the particle dispersions, how this influences their foaming behavior and illustrate the efficiency of DWS in characterizing the system.

It has been shown earlier that the adsorption of short-chain amines onto silica particles obeys the same rules as classical surfactants [44, 45]. In the beginning, there are isolated adsorption events. The adsorption of the hydrophobic amines will render the particles surface active. Above a critical surfactant concentration, the amine adsorption becomes cooperative. This leads to hydrophobic interaction between the particles and therefore, the particles aggregate.

When a dispersion of hydrophobic particles is foamed, some of the particles will go to the interface. These particles will therefore be removed from the liquid that drains out of the foam. This depletion can be quantified with density measurements, as demonstrated in this study. Boos et al showed that the surfactant depletion for classical surfactant foams is measurable [46]. The amount of particles removed from the bulk phase depends on the concentration of the amines and their chain length. With increasing hydrophobicity, the particles seem to be more capable of stabilizing a foam during the foaming procedure. Below the CAC, the foam volume increases when more particles are extracted from the bulk. This means that the number of extracted particles per unit volume of foam is constant. In turn, this supports an hypothesis that the in-plane interaction of the adsorbed particles is more important for their foaming behavior than simply the number of adsorbed particles.

Above the CAC, a drastic decrease of foam volume is found while simultaneously the number of particles that are trapped in the foam strongly increases. The reduced foamability can be explained with the reduction of free small particles, since aggregation is taking place. In a previous study, we found that aggregation significantly increases the foam life-time [44]. Large particle aggregates are easily trapped in the plateau borders and vertices [47]. These aggregates will not drain out of the foam, so the draining liquid is strongly depleted of particles. Additionally, these particles can form a gel, which slows down the dynamics of the foam.

As stated before, the following DWS data analysis is based on the model published by Crassous and Saint-Jalmes [36]. We will see that the model applies very well to our presented composite particle-foam system. In order to discuss the DWS



Figure 8. Theoretical values of the (transport) mean free path lengths l_c and l_c^* as a function of particle radius at constant silica mass concentration of 10 g L⁻¹. The l_c values are the mean distance between two scattering events in an unfoamed dispersion. The l_c^* values represent the step length after which the photon direction has been randomized in the same system.

data, it is convenient to briefly sketch the parameters of the studied system. Diffusing wave spectroscopy relies on multiple scattering of the photons travelling through the sample. The idea is that photons travel through the sample in random walk steps, like in a diffusion process. An important parameter is the transport mean free path length l^* which is the distance after which a photon has randomized its direction with respect to the incident direction. It corresponds to the random walk step length.

For unfoamed particle dispersions, the transport mean free path length can be calculated in the framework of Mie scattering theory. First, the mean free path of the colloidal dispersion l_c is calculated via $l_c = 1/\rho\sigma$ with the particle number density ρ and the particle scattering cross-section σ . The transport mean free path length is calculated as $l_c^* = l_c/(1-\chi)$ with the asymmetry parameter χ . The size of the asymmetry parameter χ is between 0 and 1. The larger the value of χ , the more directed the scattering towards certain scattering angles is. Figure 8 displays l_c and l_c^* as a function of the particle radius at constant mass concentration. With increasing radius, the particle number density ρ decreases but the scattering cross-section σ increases leading to a decrease in the mean free path l_c . For Rayleigh scatterers, the direction of a photon is randomized after a single scattering event. In this case the relation is simply $l_c^* = l_c$. In the Mie scattering regime, l_c^* is always larger than l_c . Multiple scattering events are necessary in this regime to randomize the photon direction because a single scattering event is strongly directed.

For the dispersion used in this study, we use the hydrodynamic radius determined by DLS and the mass concentration to calculate the transport mean free path $l_c \approx l_c^* = 13$ mm. This is the mean distance between two scattering events in the unfoamed dispersion. The foams in this study have a void fraction of 80% which will increase the effective colloidal transport mean free path length to $l_c^* = 65$ mm due to apparent dilution of the dispersion. We see that 65 mm is large compared to the cell width $L = 5 \,\mathrm{mm}$. It is instructive to compare the transport mean free path length of 65 mm to the length of the photon path through the foam sample. The photon path length can be calculated from the scattering properties of the foam and the thickness of the sample cell. The l_f^* of the fresh foam is in the order of 200 μ m and small compared to the cell width. There are two different transport mean free path lengths l_c^* and l_f^* in the system. The effective transport mean free path lengths l^* is calculated via

$$\frac{1}{l^*} = \frac{1}{l_f^*} + \frac{1}{l_c^*}.$$
(6)

In our study, the $1/l_c^*$ can be neglected and it follows $l^* \approx l_f^*$. We will refer to the effective transport mean free path lengths as l^* in the following discussion.

In general, the l^* depends on the bubble size and increases as coarsening of the foam matrix proceeds. Knowing the liquid fraction of $\approx 20\%$, we can estimate the mean bubble size to be in the order of 100 μ m [48], which is reasonable for the used foaming method. A photon travelling through the sample will be randomized mainly by refraction on the foam bubbles. It is possible to estimate the dominant path length of a photon through the sample by $L^2/l^* = 125$ mm. Comparing this path length to $l_c^* = 65$ mm, it is clear that a noticeable fraction of the transmitted photons will have been scattered by a particle. At the same time, it is unlikely that one will see multiple scattering caused by particles. In other words, the foam bubbles produce an isotropic field of incident photons which are likely to be scattered once from a particle before eventually exiting the sample cell.

Paths that include a particle scattering event also lead to fluctuations in the transmitted intensity on the timescale of the particle diffusion. This is the reason for the first decorrelation in figure 4(a). The second decorrelation is caused by bubble rearrangement and coalescence events. The larger the second decorrelation time, the slower the evolution of the foam matrix.

From the first decay time $\tau_{\rm B}$ of ≈ 0.23 ms an apparent particle radius can be calculated via

$$R_{\rm h} = \frac{8\tau_{\rm B}\pi kT}{3\lambda^2\eta} \tag{7}$$

with the laser wavelength λ and the liquid dynamic viscosity η . This yields an apparent radius of 28 nm. Within the experimental accuracy, this is in acceptable agreement with the DLS radius of 20 nm. For amine concentrations above the CAC, the particles start to aggregate while the mass concentration is constant. This should lead to a larger decay time. Slightly larger

decay times that indicate larger particles are observed which confirm the presence of aggregates in the foam channels.

The second decay time $\tau_{\rm R}$ increases with increasing amine concentration which indicates that the foams evolve more slowly. This can be interpreted as a stiffening of the system which is also qualitatively observed when handling the prepared foams. Foams with strongly aggregated particle networks show a time dependent increase in the $t_{\rm R}$ value, as the systems ages and gels.

We will follow up by discussing the plateau values $g_{\rm E}^*$. Theory predicts the following dependence

$$-\ln(g_{\rm E}^*) = \frac{L^2}{2l_0^* l_c} = \frac{L^2 \sigma}{3\pi l_0^* d^3} \Phi_c \tag{8}$$

with the measured transport mean free path length l_0^* denoted in the table above. The right-hand side of (8) can be used to evaluate the fits in figure 7. If both the cross-section σ and the diameter *d* of the particles are unknown, it is straightforward to calculate the ratio σ/d^3 from the slope of the curves and find e.g. the diameter by comparison with data calculated by means of Mie theory. When this is applied to the measured data, we find particle radii r_{app} as summarized in the following table.

C _n	σ/d^3 (1/m)	$r_{\rm app}~({\rm nm})$
$\overline{C_5}$	5617	28.8
C ₆	6776	30.8
C ₇	7019	30.9
C ₈	6444	30.3

These values are larger than the hydrodynamic radii probed by DLS. Nonetheless, it should be noted that they compare very well to the apparent radii of 28 nm extracted from the $\tau_{\rm B}$ values. Both methods which were presented to obtain a measure for the particle size in the foam are different in their approach. One uses information from the decorrelation time, the other one is based on the total amount of decorrelation. Modelwise there is no correlation between that information.

Another aspect of the information in the g^* values shall be addressed. If we assume that the silica particles in the foam channels start to aggregate, their l_c value would decrease as depicted in figure 8 and explained earlier. Equation (8) shows the dependence of the plateau value g_E^* on l_c . It turns out that aggregation should lead to a decrease of the plateau value g_E^* . In our experiments, this decrease is not observed. The opposite is found, in samples with strong aggregation the plateau is nearly absent. An easy explanation is the gelation or settling of the aggregates in the foam structure. As these large aggregates do not move any longer, they cannot cause any decorrelation in the transmitted beam intensity. Only freely diffusing particle (aggregates) contribute to the fast decorrelation signal in figure 4(c).

5. Conclusion

We investigate the structure and dynamics of an aqueous particle stabilized foam. Our data suggest that the foam structure and dynamics depend on the interfacial particle interaction as well as the particle aggregation state in the bulk foam liquid.

For all studied alkyl chain lengths, there exists a characteristic amine concentration that leads to immediate particle aggregation. Below this threshold concentration, particles become more efficient foam stabilizers as the amine concentration is increased. The amine adsorption leads to increased hydrophobicity of the particles. A decrease in the foam rearrangement time is found, as the hydrophobicity of the particles is increased. The nanoparticle diffusion can be probed by DWS and their size can be determined in the foam. When two of the three parameters particle mass concentration, particle size and foam liquid fraction are known, the third can be conveniently determined by means of DWS. Two independent approaches to determine the particle size in the foam were validated successfully.

When the particle hydrophobicity is increased to a degree at which bulk aggregation starts, the foam structure gels as reflected by the long foam rearrangement times. The arrest of single particle dynamics is seen by the absence of a strong particle induced fast decorrelation in the autocorrelation function.

The present paper illustrates the power of the diffusing wave spectroscopy technique to characterize complex composite materials that include several largely separated length scales. It illustrates how a component of the matrix can be probed optically without the need for the sample to be transparent or optically homogeneous.

We hope this study stimulates further research in the field of food and soft matter science to yield a better understanding of particle stabilized foams.

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