Erschienen in: Colloids and Surfaces / A: Physicochemical and Engineering Aspects ; 473 (2015). - S. 40-45

Studying foam dynamics in levitated, dry and wet foams using diffusing wave spectroscopy

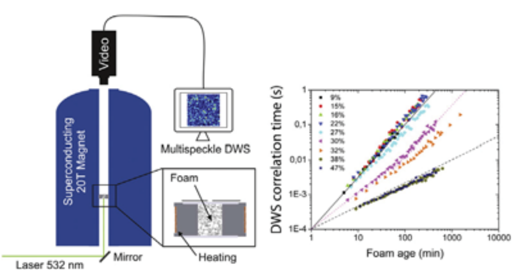
Nathan Isert[a], Georg Maret[a,*], Christof M. Aegerter[b]

[a] *Fachbereich Physik, Universität Konstanz, Universitätsstrasse 10, 78457 Konstanz, Germany*
[b] *Physik-Institut, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland*

HIGHLIGHTS

- Coarsening dynamics of foams studied by multi-speckle diffusing wave spectroscopy.
- Magnetic levitation allows a large range of liquid fractions to be studied for hours.
- Cross over from Neumann to Ostwald regime at liquid fraction around 30%.
- In dry foams intermittent bursts of activity signal collective bubble rearrangements.
- In wet foams bubbles move ballistically with random collisions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Foam dynamics
Levitation
Diffusing wave spectroscopy

ABSTRACT

We use diffusing wave spectroscopy to study the microscopic dynamics of foams. These foams are levitated diamagnetically, such that very high liquid fractions can be achieved. We find that at low liquid fraction the dynamics is dominated by local rearrangements, whereas at high liquid fraction the movement of bubbles is ballistic and large scale rearrangements are absent. This change in the microscopic dynamics coincides with a change in the scaling of coarsening on increasing the liquid fraction that we have found earlier.

1. Introduction

The dynamics of foams has been studied intensely due to the fact that they are interesting model systems for non-equilibrium dynamics as well as important in several industrial applications [1]. However due to the drainage of fluid in response to gravity [2], these studies have been mostly limited to foams containing little liquid, i.e. at liquid fractions below 20% [3–5,7,6,8,9]. Recently, we have studied foams at very high liquid fraction (up to 50%) using diamagnetic levitation to circumvent the problem of drainage. In this way, the lifetime of wet foams was strongly increased [10]. Alternatively, experiments are planned to be carried out on the international space station, which would also allow the study of very wet foams [11].

The study of wet foams is of particular interest because at liquid fractions around 30% a transition in the foam dynamics is predicted due to the fact that at these liquid fractions the gas bubbles start to lose their contacts [11–13]. This not only changes the dynamics of gas exchange between bubbles, which is of crucial importance for the coarsening behaviour, but also the movement of bubbles is

* Corresponding author. Tel.: +49 7531884151; fax: +49 7531883090.
E-mail address: Georg.Maret@uni-konstanz.de (G. Maret).

qualitatively changed leading to a liquid like behaviour of the foam. Here, we will address the question of the local bubble dynamics in diamagnetically levitated dry and wet foams using diffusing wave spectroscopy (DWS) [14,15,8]. In particular using multi-speckle DWS [18] based on a fast camera, we are studying the time dependence of local movement of the scatterers on time scales of several seconds [17]. We find large local rearrangements in dry foams [8] contrasting with a more continuous dynamics in very wet foams.

Before discussing the results, we will discuss the basis of diamagnetic levitation and the potential landscape for residual accelerations in our setup [19,20], as well as the fundamentals of DWS with an emphasis on multi-speckle DWS [14,15,17]. Then we will present results on the averaged dynamics, which corresponds well with our earlier results on the transition in coarsening dynamics [10]. Finally, we will discuss the spatio-temporally local dynamics for both wet and dry foams.

2. Diamagnetic levitation

Due to the diamagnetism of water it is possible to stably levitate it in a strong enough magnetic field gradient. As described in [21,22], two conditions have to be fulfilled in order to achieve a stable levitation. These correspond to a potential minimum in both the vertical (z) and the radial (r) directions. This potential energy density landscape can be obtained for a given solenoid to be: $E_{pot}(r, z) = \mu_0 \chi H^2(r, z) + \rho g z$. Here, χ is the magnetic susceptibility and ρ is the density of the material studied. In order to have a minimum in this potential energy, the magnetic susceptibility has to be negative, such that only diamagnetic substances can be levitated. In addition, levitation is achieved at a certain height (determined by the ratio of ρ to χ), where the radial gradient of the magnetic field of the solenoid has to be positive. In our experiments, we use a superconducting solenoid capable of reaching a maximum field of 18 T and a vertical room temperature bore with a diameter of 4 cm [19]. The field distribution of the solenoid leads to potential energy landscapes for levitation shown in Fig. 1 [19,20]. The residual accelerations in the central area can be easily obtained from the slope of this plot and are less than 0.001 g in all directions in the innermost volume of 1 cm^3, i.e. better than the jitter in parabolic flight experiments. Therefore we use a sample-cell of a height of 1.2 cm and a diameter of 1.7 cm to ensure a homogeneous levitation of the entire sample.

The samples we use consist of a mixture of water and sodium dodecyl sulfate (SDS), containing 8% of SDS by weight that is foamed with nitrogen gas using two connected syringes connected by a thin tube [23,19]. The foams thus created have an average initial bubble size of 100 μm and a large polydispersity of more than 50%, as can be seem in Fig. 1 of Ref. [10]. The liquid fraction is controlled by the initial ratio of gas to liquid in the two syringes, which can be controlled to an accuracy of 1–2%. On foaming the sample, the gas is compressed, leading to a systematic underestimation of the foams liquid fraction from the controlled initial liquid fraction. The liquid fractions quoted in the following always refer to the initial liquid fraction. From an estimation of the pressure exerted on the gas after foaming the underestimation of the liquid fraction is around 5%.

3. Diffusing wave spectroscopy

Diffusing wave spectroscopy is a version of dynamic light scattering that can be applied to multiply scattering samples and gives information about movements on the nm-scale in such samples [14,15]. For this purpose, we illuminate the sample with a Coherent Verdi CW laser at a wavelength of 532 nm and a power of 100 mW. The transmitted light is collected with an optical fibre and a photomultiplier and a correlator, which is averaged over a few minutes for single speckle measurements and with a LaVision high speed star 5 (HSS5) camera at a frame rate of 1000 fps capturing the dynamics of several speckles for a time frame of up to 10 s. Since DWS is a multiple light scattering technique, the information obtained on the scatterer displacements, while being on very small spatial scales, is averaged over the whole sample. In single speckle measurements, it is also averaged over long times in order to have reliable statistics for determining the correlation function

$$g_2(t) = A \exp(-2k^2 \langle \delta r(t)^2 \rangle L^2 / l^{*2}) + 1, \qquad (1)$$

where $k = 2\pi/\lambda$ is the wavenumber of the incident light, l^* is the transport mean free path of the light and L is the sample thickness [15]. $\langle \delta r(t)^2 \rangle$ is the mean square displacement of the scatterers, which is given by $\langle \delta r(t)^2 \rangle = 6Dt$ in case of Brownian motion with diffusion constant D and by $\langle \delta r(t)^2 \rangle = (\Gamma l^* k)^2/30 \cdot t^2$ for shear flow with shear rate Γ [16].

In order to access fast rearrangements in a foam, where the dynamics of the sample only takes place in short bursts, the temporal resolution of a single speckle DWS experiment is not sufficient. For this purpose, we use multi-speckle DWS, where we follow many speckles using a fast camera, as shown in Fig. 2 [17]. Averaging the correlation functions of many speckles spatially, each individual pixel is treated as a single correlator for which temporal averaging can be reduced to just one second, while spatial averaging provides the statistics. To study fast dynamics such as they are induced by bubble rearrangement events the recorded frames were post-processed using this multi speckle statistics with a shifting starting time and a constant time average. The change in dynamics can be attributed to the shift, which in this case was 50 frames, i.e. 50 ms.

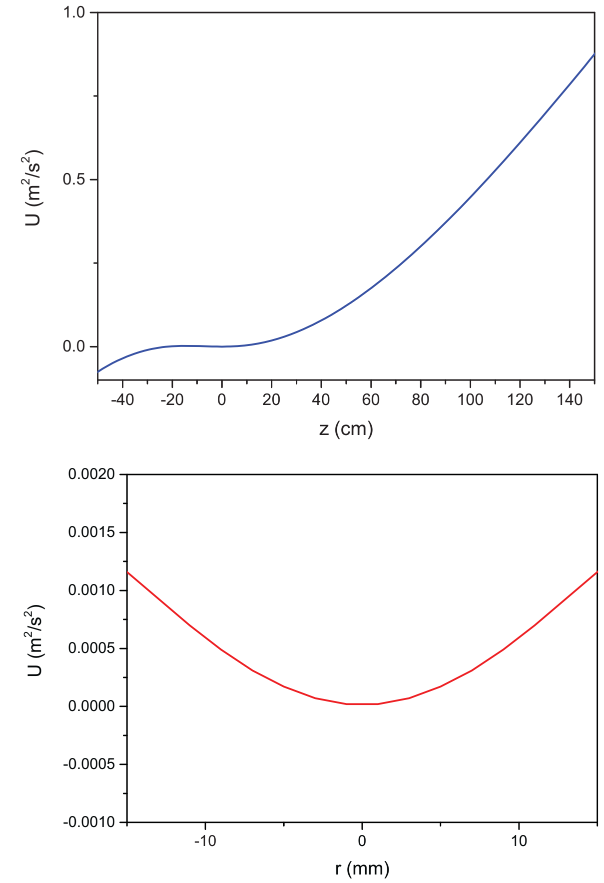


Fig. 1. Potential energy landscape in the vertical (z) and radial(r) directions. As can be seen, up to distances of a few mm in both r and z, the residual accelerations from these potentials are less than 0.001 g.

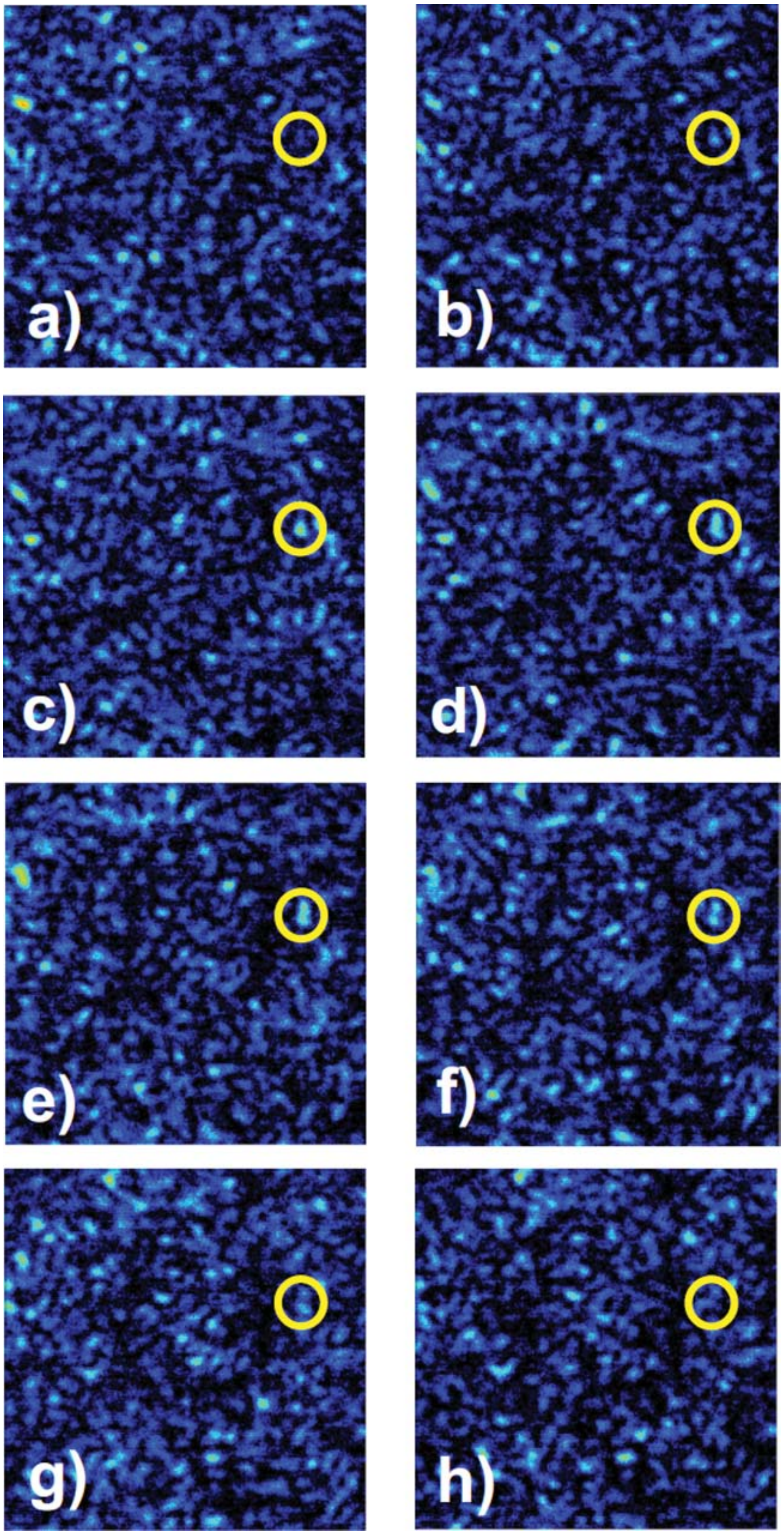


Fig. 2. Speckle pattern of a foam with 20% liquid fraction at an age of 100 min viewed with a high speed camera. The different images show subsequent frames spaced by 10 ms of the same speckle pattern. This can cover the dynamics of the changes in the speckle pattern as evidenced by the circled speckle that appears and disappears in the covered time-frame.

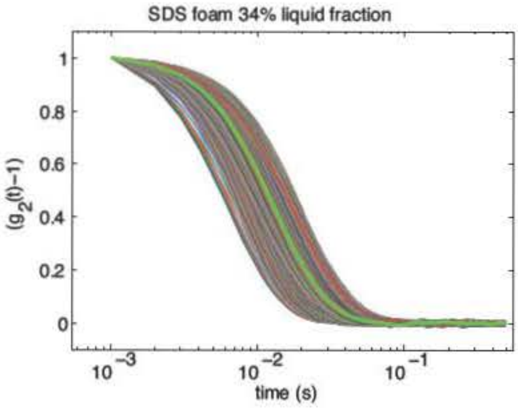


Fig. 3. Correlation function from multiple speckles obtained with a fast camera. The different curves correspond to different times in the foam on the scale of seconds showing large fluctuations in the temporal dynamics of the scatterers.

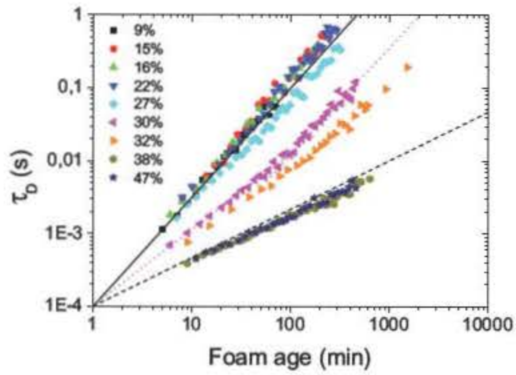


Fig. 4. DWS correlation times obtained from integrating g_2 for several foams as a function of foam age. At low liquid fraction, the correlation time scales with age$^{3/2}$ (full line), whereas at high liquid fraction it scales as age$^{2/3}$ (dashed line). Around liquid fractions of 30%, close to the transition, two regimes corresponding to the limiting cases can be seen.

Therefore it becomes possible to identify large rearrangements of bubbles in dry foams. These variations can be seen in Fig. 3, where the correlation functions averaged over many speckles taken at different but small averaging times reveal large fluctuations of the DWS correlation time τ_D. Before we discuss these fluctuations of τ_D we turn first to the ageing behaviour of τ_D averaged over longer times (but still short compared to the ageing time scale).

4. Results

As discussed above, it is predicted that foams show a qualitative change in the coarsening dynamics with increasing the liquid fraction above roughly 30%. We have shown this by studying the diffuse transmission from levitated foams as a function of foam age and liquid fraction, where we have found a transition between two distinct coarsening regimes [10]. The diffuse transmission, giving a measure of the mean free path l^* [24] and hence the mean bubble size r [25,26] shows a change in age scaling exponent from 1/2 to 1/3, which needs several decades of dynamic range to be separated experimentally. Therefore at intermediate liquid fractions, only an intermediate exponent could be determined [10]. When studying the local dynamics via DWS and the corresponding decay time of the correlation function, the spread in scaling exponent is much bigger. As can be seen from Eq. (1), the characteristic decay time τ_D depends on l^{*2} and $1/\langle\delta r^2\rangle$. In the dry case the dynamics is Brownian, $\langle\delta r^2(t)\rangle \propto t$, probably due to tiny random motions originating from thermally fluctuating film surfaces and/or random relaxation events due to distributed stresses [10]. At higher liquid fractions $\langle\delta r^2(t)\rangle$ progressively crosses over to ballistic motion $\langle\delta r^2(t)\rangle \propto t^2$, probably due to the progressive onset of very slow convective motions which give rise to small relative displacements of individual bubbles [10]. Note that, whatever the shear rate Γ, diffusive motion will always dominate $\langle\delta r^2(t)\rangle$ at times $t \ll \tau_c \approx D/(l^{*2}\Gamma^2)$ [16]. Therefore, as small (convective) shear may appear more easily at higher liquid fractions, the temporal cross over of $\langle\delta r^2(t)\rangle \propto t^2$ at large t to $\langle\delta r^2(t)\rangle \propto t$ at small t moves with increasing liquid fraction through the time window of the DWS experiment set by $\langle\delta r^2(t)\rangle \approx l^{*2}/(Lk)^2$. We thus expect that τ_D crosses over from $\tau_D \propto l^{*2}/(k^2L^2D)$ (dry case) to $\tau_D \approx \tau_c$ (wet case) and only at higher shear rates when τ_c moves out of the small t side of the DWS time window we expect $\tau_D \propto 1/(k\Gamma L)$.

In order to arrive at the scaling of τ_D with age, we use the fact that l^* scales with bubble size r. Therefore, in the diffusive regime, τ_D scales as r^3 and hence $\tau_D \propto age^{3/2}$ for dry foam. For wet foams and $\tau_D \approx \tau_c$ we obtain $\tau_D \propto l^{*2}/(Dk^2L^2) \propto r^2 \propto age^{2/3}$. Such a change in age-exponent from 3/2 to 2/3 is indeed observed in Fig. 4, where the age dependence of the DWS correlation time is shown for several foams ranging in liquid fraction from 9% to 47%. At intermediate liquid fractions (between 27% and 32%), the two regimes of scaling can be seen with distinct exponents as τ_c crosses the DWS time window.

The results of Fig. 4 come from single speckle DWS and thus average the dynamics over long time frames. As discussed above, when averaging over shorter times, large fluctuations can be seen, which we study in the following using multi-speckle DWS [17]. Here, we obtain the decay time from determining the correlation function from several speckles and averaging those over a time frame of 50 ms. With this we obtain good enough statistics for a determination of g_2 and the corresponding decay time on a 50 ms time scale. Since we obtain these data from movies of up to a minute, we can study the time dependence of the decay time that in Fig. 4 was averaged over completely. This is shown in Figs. 5 and 6 for two foams with liquid fractions of 19% and 34%, respectively. In addition, the time dependence of the decay time is shown for several foam ages, showing the effect of coarsening on the dynamics. For comparison, the figures also contain the average decay time, which shows the same dependence as that from single speckle DWS shown in Fig. 4.

Comparing the dynamics for the two different liquid fractions, one observes that for relatively dry foams, the dynamics is dominated by large, intermittent bursts of activity, in between which the dynamics is very slow, corresponding to an almost stationary

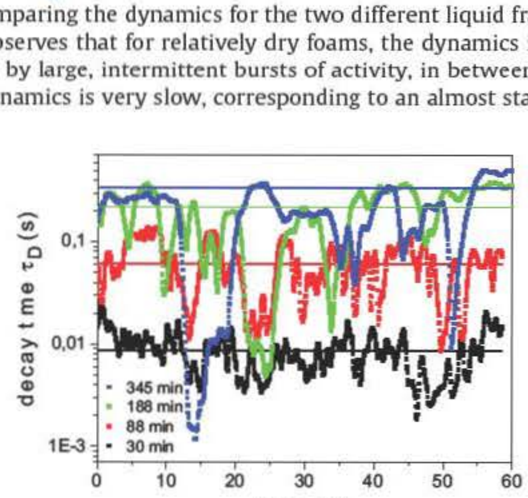


Fig. 5. Temporal dependence of the DWS decay time for a foam of 19% liquid fraction for several ages of the foam. In addition to an overall increase of the average decay time due to the coarsening of the foam, a marked change in the dynamics can be seen. At late age, the dynamics is dominated by intermittent burst of activity corresponding to large scale rearrangements of bubbles, which decrease in frequency as the foam coarsens.

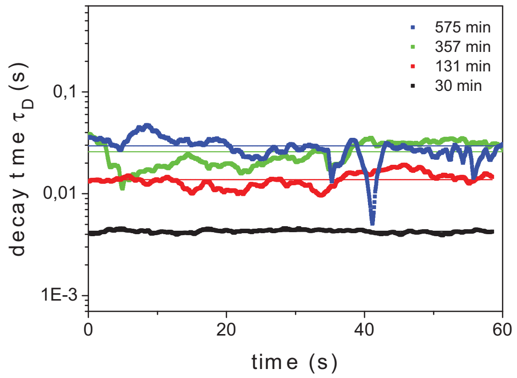


Fig. 6. Temporal dependence of the DWS decay time for a foam of 34% liquid fraction for several ages of the foam. In contrast to the relatively dry foam of Fig. 5, the dynamics is here not dominated by single events, but rather by random fluctuations. In addition, the time scale of the decay time is much faster, connected to the ballistic motion of bubbles between collisions.

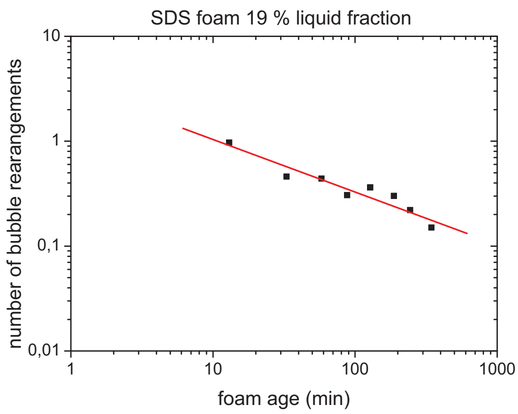


Fig. 7. The rearrangement frequency in a foam of 19% liquid fraction. The frequency scales with the foam age $^{-1/2}$, as indicated by the solid line. The rearrangement frequency is given in s^{-1}

foam. The frequency of these bursts decreases with age of the foam such that in the oldest foam in Fig. 5, the bursts of activity are well separated. The frequency of such large rearrangements in the foam can be obtained from this time dependence and is shown in Fig. 7 as a function of age. The straight line indicated in the figure corresponds to a scaling of the rearrangement rate $\propto$ age$^{-1/2}$, which is similar to what Durian et al. [27] found in shaving cream. This would correspond to von Neumann coarsening dynamics when the overall dynamics probed by DWS is solely due to large scale rearrangements, which give rise to an overall diffusive dynamics with $\langle \delta r^2 \rangle \propto t$ as is indeed observed [10].

In contrast, the dynamics of the decay time for wet foams is markedly different as there are no large scale bursts of activity and the overall heterogeneities are rather smooth. Also, the overall increase in the decay time is much slower as given by the slower coarsening law valid in the wet limit. The overall dynamics here is rather given by the ballistic motion of bubbles in between collision events, which take place at the short time scales picked up by DWS [10]. Thus there are no large scale rearrangements, which is clearly reflected in the time dependence of the decay times and no rearrangement frequency can be determined. Again, this dynamics points strongly to a state of the wet foam, where bubbles are separated and perform ballistic motion.

5. Conclusions

In conclusion, we have shown that the coarsening dynamics of foams of various liquid fractions can be studied in great detail using multi-speckle DWS. The foams are levitated allowing a large range of liquid fractions to be studied, in particular, we can study foams of liquid fractions corresponding to separated bubbles rather than solid foams. As we have found previously [10], at a liquid fraction of about 30%, the coarsening dynamics shows a marked change corresponding to the separation of bubbles. Here we study this transition in the local dynamics, where we find that the decay time of g_2 shows a change in the dynamics as found previously between a von Neumann like [12] to an Ostwald-like regime [13]. At intermediate liquid fraction however, the larger spread in the corresponding scaling exponents allows for a determination of a cross-over in dynamics in a single foam with age, as the increase in bubble size with coarsening will lead to an eventual contact of the bubbles and therefore a change in the coarsening dynamics.

In addition, we have studied the non-local dynamics at intermediate time scales using multi-speckle DWS [17], where we find that at low liquid fractions, the dynamics is dominated by intermittent bursts of activity, which we associate to large scale rearrangements of bubbles, whose frequency decreases with foam age [27]. For wet foams, in contrast, no such rearrangements can be seen and the overall dynamics corresponds to that of ballistically moving slowly convecting bubbles.

Acknowledgments

This work was funded by DFG in the context of the IRTG 667 on Soft Matter Physics of Model Systems as well as the Landesstiftung Baden-Württemberg and the Swiss National Science Foundation.

References

[1] D. Weaire, S. Hutzler, The Physics of Foams, Oxford University Press, 1999.
[2] S.A. Koehler, et al., Dynamics of foam drainage, Phys. Rev. E 58 (1998) 2097.
[3] J.A. Glazier, S.P. Gross, J. Stavans, Dynamics of two-dimensional soap froths, Phys. Rev. A 36 (1987) 306.
[4] C.P. Gonatas, et al., Magnetic resonance images of coarsening inside a foam, Phys. Rev. Lett. 75 (1995) 573.
[5] J. Lambert, et al., Coarsening foams robustly reach a self-similar growth regime, Phys. Rev. Lett. 104 (2010) 248304.
[6] S. Hilgenfeldt, S.A. Koehler, H.A. Stone, Dynamics of coarsening foams: accelerated and self-limiting drainage, Phys. Rev. Lett. 86 (2001) 4704.
[7] S. Hutzler, D. Weaire, Foam coarsening under forced drainage, Philos. Mag. Lett. 80 (2000) 419.
[8] D.J. Durian, D.A. Weitz, D.J. Pine, Multiple light-scattering probes of foam structure and dynamics, Science 252 (1991) 686.
[9] A.E. Roth, C.D. Jones, D.J. Durian, Bubble statistics and coarsening dynamics for quasi-two-dimensional foams with increasing liquid content, Phys. Rev. E 87 (2013) 042304.
[10] N. Isert, G. Maret, C.M. Aegerter, Coarsening dynamics of three dimensional levitated foams: from wet to dry, Eur. Phys. J. E 36 (2013) 116.
[11] D. Langevin, M.Vignes-Adler, Microgravity studies of aqueous wet foams, Eur. Phys. J. E 37 (2014) 16; V. Vandewalle et al. Foam stability in microgravity, J.Phys. Conf.Ser. 327 (2011) 012024; A. Saint-Jalmes, S. Marze, M. Safouane and D. Langevin, Foam experiments in parabolic flights: development of an ISS facility and capillary drainage experiments, Microgravity sci. technol. 18, (2006) 22.
[12] J. von Neumann, Written discussion of grain shapes and other metallurgical applications of topology, in: C. Herring (Ed.), Metal Interfaces, 1952, p. 108.
[13] W. Ostwald, Ueber die vermeintliche Isomerie des roten und gelben Quecksilberoxyds und die Oberflaechenspannung fester Koerper, Z.Phys. Chem. 34 (1900) 495; I.M. Lifshitz and V.V. Slyozov, The kinetics of precipitation from supersaturated solid solutions, J. Phys. Chem. Solids 19 (1961) 35; C. Wagner, Theory of the aging of precipitates by dissolution-reprecipitation (Ostwald ripening), Z. Elektr. Inf.-Energietech. 65 (1961) 581; A. J. Markworth, The kinetic behavior of precipitate particles under Ostwald ripening conditions, Metallography 3 (1970) 197; W.W.Mullins, The statistical self-similarity hypothesis in grain growth and particle coarsening, J. Appl. Phys. 59 (1986) 1341.
[14] G. Maret, P.E. Wolf, Multiple light scattering from disordered media. The effect of brownian motion of scatterers, Z. Phys. B 65 (1987) 409.

[15] D.J. Pine, D.A. Weitz, J.X. Zhu, E. Herbolzheimer, Diffusing-wave spectroscopy: dynamic light scattering in the multiple scattering limit, J. Phys. 51 (1990) 2101.

[16] D. Bicout, G. Maret, Multiple light scattering in Taylor–Couette Flow, Phys. A 210 (1994) 87.

[17] S. Cohen-Addad, R. Höhler, Bubble dynamics relaxation in aqueous foam probed by multispeckle Diffusing-Wave Spectroscopy, Phys. Rev. Lett. 86 (2001) 4700.

[18] L. Cipelletti, D.A. Weitz, Ultralow-angle dynamic light scattering with a multi-speckle, multitau correlator, Rev. Sci. Instrum. 70 (1999) 3214.

[19] N. Isert, Dynamics of Levitated Foams. (Ph.D. thesis), University of Konstanz, 2013.

[20] C.C. Maass, N. Isert, G. Maret, C.M. Aegerter, Experimental investigation of the freely cooling granular gas, Phys. Rev. Lett. 100 (2008) 248001.

[21] W. Braunbeck, Freies Schweben diamagnetischer Koerper im Magnetfeld, Z. Phys. 112 (1939) 764.

[22] M.V. Berry, A.K. Geim, Of flying frogs and levitrons, Eur. J. Phys. 18 (1997) 307.

[23] A. Saint-Jalmes, M.U. Vera, D.J. Durian, Turbulent method of foam production: new results on free-drainage vs. liquid content, Eur. Phys. J. B 12 (1999) 67.

[24] P. Sheng, Introduction to wave scattering, in: Localization and Mesoscopic Phenomena, Academic Press, 1995.

[25] M.U. Vera, A. Saint-Jalmes, D.J. Durian, Scattering optics of foam, Appl. Opt. 40 (2001) 4210.

[26] A.S. Gittings, R. Bandyopadhyay, D.J. Durian, Photon channelling in foams, Europhys. Lett. 65 (2004) 414.

[27] D.J. Durian, D.A. Weitz, D.J. Pine, Scaling behavior in shaving cream, Phys. Rev. A 44 (1991) R7902.