Sonochemistry and bubble dynamics

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ABSTRACT

The details of bubble behaviour in chemically active cavitation are still not sufficiently well understood. Here we report on experimental high-speed observations of acoustically driven single-bubble and few-bubble systems with the aim of clarification of the connection of their dynamics with chemical activity. Our experiment realises the sonochemical isomerization reaction of maleic acid to fumaric acid, mediated by bromine radicals, in a bubble trap set-up. The main result is that the reaction product can only be observed in a parameter regime where a small bubble cluster occurs, while a single trapped bubble stays passive. Evaluations of individual bubble dynamics for both cases are given in form of radius-time data and numerical fits to a bubble model. A conclusion is that a sufficiently strong collapse has to be accompanied by non-spherical bubble dynamics for the reaction to occur, and that the reason appears to be an efficient mixing of liquid and gas phase. This finding corroborates previous observations and literature reports on high liquid phase sonochemical activity under distinct parameter conditions than strong sonoluminescence emissions.

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1. Introduction

Acoustic cavitation is widely used to cause, trigger, promote, or influence chemical reactions in liquid–gas systems [1,2]. However, the microscopic dynamics of bubbles in sound fields depends on many parameters and details of their environment, e.g. acoustic frequency and pressure, liquid and dissolved gas properties, neighbouring bubbles or boundaries. Thus it is clear that "the" acoustic cavitation bubble does not exist, but many variants in terms of their properties like life time, collapse compression rate, or collapse symmetry. In multi-bubble environments one typically has to deal with different types of bubble dynamics, and groups of similar bubbles can be described as "bubble populations" [3,4]. With respect to sonochemistry, it is still not sufficiently well understood what type of bubble dynamics leads to what kind of activity, not to speak of a sufficient control over the desired bubble behaviour. This work tries to contribute to a better understanding of this issue. In an experiment where the chemical activity of a single trapped bubble can be externally controlled, the bubble dynamics is recorded by a high-speed camera. As activity measure we use the fumaric/maleic acid isomerization which involves the liquid phase and results in an insoluble solid product [5,6]. Chemistry and bubble behaviour are correlated, evaluated with help of a numerical model, and interpreted. A discussion is given which generally refers to reactions including liquid phase reactants.

Sonochemical systems are generically multi-bubble environments, where in virtually all cases the chemical reactions take place in connection with the strongly and rapidly compressed and heated interior of collapsing bubbles. Consequently, the reactions occur in many individual events isolated in space and time which renders sonochemistry as an inherently inhomogeneous process – in spite of a potentially homogeneous or smoothly varying primary sound field. Indeed, the phrase "sono" and the commonly used reaction symbol ")))" which represents the acoustic wave are actually not valid, as is well known of course for a long time [2]. If we wanted to replace the wrong notation by something more adequate, the reaction mediated by cavitation bubble collapse might be indicated for instance by "Oo.". However, in the following we show that even the notion of "bubble collapse chemistry" might need a specification with respect to what type of bubble collapse promotes the reaction, and caricatures like "OB3" (jetting collapse), "O8:" (splitting collapse), or ":öÖö:" (strongly interacting few-bubble cluster) could possibly give a more exact picture of the situation.

The idea to leave the multi-bubble environment and to prepare an isolated, acoustically driven and chemically active bubble came up after the seminal experiments with acoustic bubble traps in the

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context of single-bubble sonoluminescence (SBSL) [7]. The first incarnations of such "single-bubble sonochemistry" (SBSC) systems with a visible chemical reaction product were realised by Lepoint et al. [8,9]. The chemical reactions in these experiments were performed in acoustic bubble traps driven in the 20 kHz frequency region, and they yielded products of high optical contrast which made them perceivable by the naked eye. Namely, in a Weissler type of reaction in an aqueous CCl_4 solution, $Cl·$ radicals were produced which reacted further reducing iodide to iodine. A complex of iodine with starch resulted in the well-known violet colour that appeared as a streak from the bubble position if chemical activity was present [8]. A variant of this experiment has been repeated later by Troia et al. [10] who showed that indeed a bubble, driven sufficiently strong, is causing the reaction in the presence of CCl_4, and that the liquid phase should enter the hot gas phase somehow. The other type of chemical probe was the reaction of CS_2 dissolved in water. Here, insoluble elementary sulphur resulted, apparently from pyrolysis and clearly visible as a white mist in the solution. Again, the product appeared as a streak on one side of the bubble position (and not as a homogeneous cloud diffusing outward spherically, as one might have been expected). This phenomenon was attributed to the specific flow field around the bubble if the volume oscillation would be synchronous to a translational oscillation of bubble position [9,11]. Fast bubble translation and strong collapse should also cause non-spherical bubble shapes, in particular jetting [12,13]. A jetting collapse is expected to increase the induced directed flow around the bubble significantly, and the observed flows close to levitated bubbles have been interpreted as an indication of this [14].

Already in the early work on SBSC, an unexpected but clear dissimilarity of bubble activity regimes of strong sonoluminescence emissions and of high sonochemical yield were stressed. Particular activity from the levitated bubble was noted in the so-called "shuttlecock" state [7,8]. Coarse observations of this case suggested the presence of a small bubble cloud instead of a single one, but very detailed images apparently have not been obtained.

In a subsequent work, Didenko and Suslick presented chemical dosimetry from a levitated single bubble [15] where the production rate of nitrite ions, hydroxyl radicals, and photons from sonoluminescence were measured and set in relation. In this case, a strong correlation of chemical yields and light emissions from the bubble occurred, which is in apparent distinction to Lepoint's findings. No specific bubble dynamics regimes nor imaging were reported by Didenko et al., but from the strong SBSL emissions and from the contrast to Lepoint's results one can suppose that indeed only a single bubble was active. A second study on ion yields from SBSL bubbles was published by Koda et al. [16], and the reported formation rates were comparable to those from [15]. No correlation to light emission and no variation of driving parameters have been presented there. On the other hand, the ratio of nitrite to nitrate ions and of the energetic yield efficiency has been compared to previous results from multi-bubble systems. The authors found a deviating ion ratio and a significantly lower efficiency in their single-bubble system. However, the variation of experimental parameters like ultrasonic frequency and power density in the compared literature was very large, and a "fair" comparison might be doubted.

In another early work, Hatanaka et al. employed sono-chemiluminescence from luminol as a measure of chemical activity in a single-bubble set-up [17]. While the luminol reaction is rather complex [18] and can contain time retarding elements [4], it can be used as an indicator of hydroxyl radical production. In Hatanaka's work, again different bubble dynamics regimes were reported, and in concordance with Lepoint the chemical activity (in terms of luminol emission strength) appeared mainly for "dancing" bubbles and not for a single stabilized one (while

standard black body-like sonoluminescence emissions behaved oppositely). The dancing was interpreted as "unstable collapse", and this dynamical feature was conjectured as a "key parameter" for the occurrence of the luminol reaction.

While the briefly summarized previous work demonstrates that single-bubble "sono" chemistry is feasible and a potential tool for gaining a clearer picture of the connection of bubble dynamics and chemical reactions, the results might appear partly inconsistent or incomplete. Unfortunately this excellent experimental method of isolation of active bubbles has not been exploited very frequently in the past. Therefore we report here on a further application of SBSC using a reaction which involves the liquid (aqueous) phase, namely the isomerization reaction of fumaric acid from maleic acid, mediated by bromine radicals from dissolved dibromomethane. This reaction has been demonstrated to be feasible in a single-bubble set-up before by Troia et al. [6].

2. Experimental section

Our bubble trap set-up consists of a rectangular glass cell of dimension $6 \times 6 \times 10(h)$ cm^3 and is driven around 18.5 kHz by a submerged ultrasonic horn (diameter 19 mm) dipping in from the open top. Sufficiently low power ensures that no cavitation at the horn tip occurs. A single bubble is generated by a submerged Ni–Cr heating wire. The bubble can be trapped near the cuvette centre for sufficiently degassed liquid, which is an aqueous 2 M solution of maleic acid saturated with dibromomethane CH_2Br_2 [6]. The gas content is adjusted before the experiment to about 25–30% air saturation by stirring under reduced atmospheric pressure. During the measurements, the air content of the liquid slowly rises again due to re-gassing through the free surface and possibly reaches up to 40% saturation.

Colour photographs of the system were taken by a digital camera (Canon G12), and fast sequential recordings could be obtained using a digital high-speed camera (Photron Fastcam SA5) with white LED background illumination. Magnifying optics (Infinity K2) was used to reach sufficient spatial resolution.

The chemical activity refers to production of bromine radicals from CH_2Br_2 which in turn leads to the isomerization from maleic to fumaric acid [5,6]. The virtually insoluble fumaric acid forms a visible whitish filament in the water which emerges from the cavitation bubble site and is slowly transported by liquid motion; see Fig. 1. As the experimental conditions are quite similar to those reported in [6], we suppose that the emerging product is identical (i.e., indeed fumaric acid), and no specific chemical tests have been made to prove this. We cannot rule out other chemical reactions in or at the bubble when no white streak occurs, for instance a fumaric acid production too low to detect, or water vapour decomposition with OH· radical production. In the following, our notion of "chemically (in)active" bubble(s) always denotes production of a fumaric acid filament.

3. Results

3.1. Observations

By changing acoustic driving parameters, i.e. the exact frequency or the amplitude, it is possible to switch the chemical activity of a trapped bubble in the cuvette (i.e. a whitish streak does either clearly occur or not). For such a transition from a chemically inactive bubble towards an active one, for instance by a slight increase of the driving pressure, the bubble behaviour is recorded just before and just after the transition. It was striking to see each time a change from a solitary bubble to a small ensemble of bubbles. While a single inactive bubble might show slight collapse
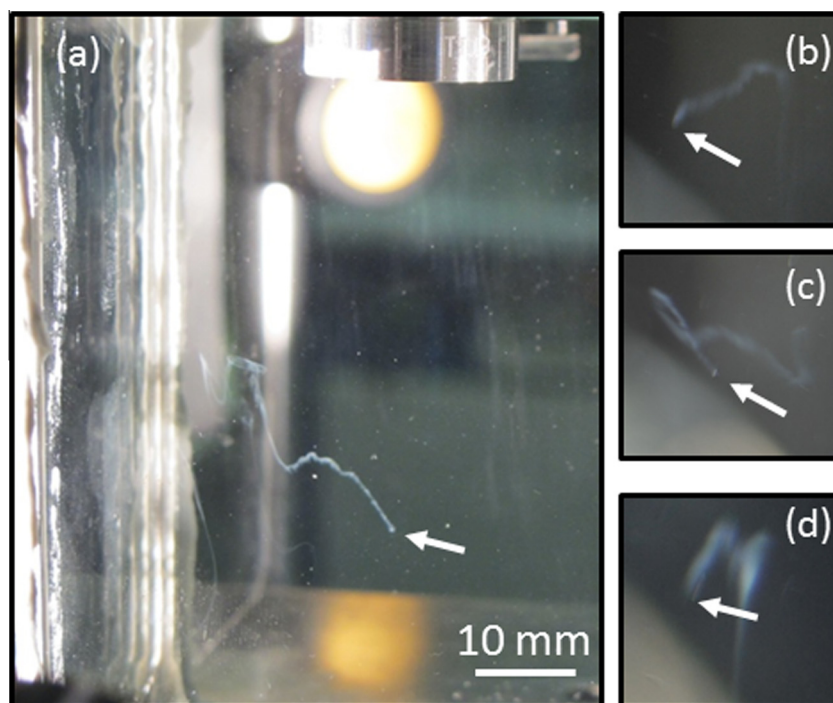
Fig. 1. Side view of the cuvette (a) with chemically active bubble in the lower centre (arrow) and sonotrode tip on top (diameter 19 mm). The clearly visible white trace of chemical product is transported by liquid flow first in upper left direction and then descends closer to the container wall. Traces of chemical product in different realisations of the experiment are shown in (b), (c) and (d) where the arrow points to the respective position of the active site.
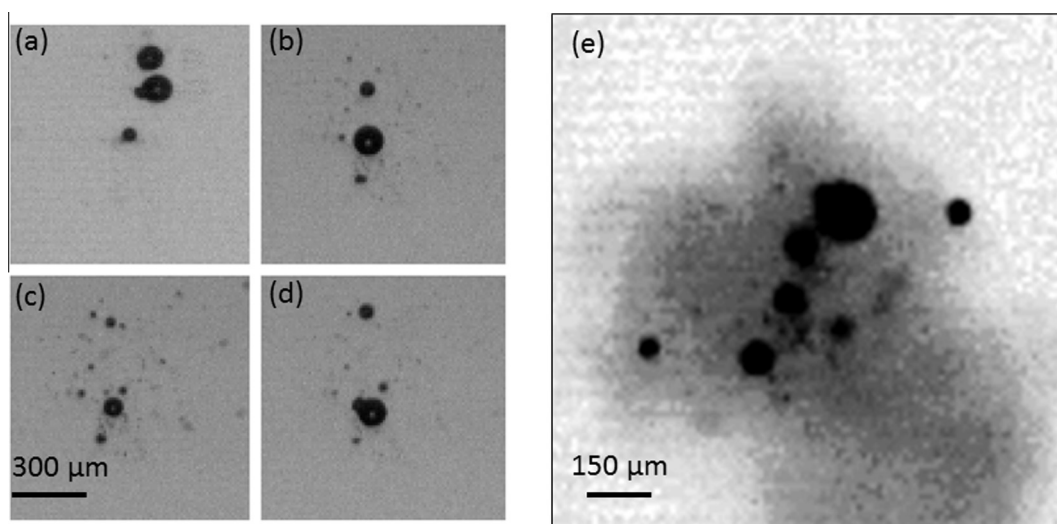

Fig. 2. Images of chemically active bubble clusters (frames from high-speed recordings of different experiments, scale given). In (e) the darker halo corresponds to the solid chemical product fumaric acid (picture contrast and resolution enhanced). In the other frames (a)–(d), the fumaric acid is not visible on this scale, although a macroscopic whitish streak is produced by the clusters.

deformations and at times ejection of a small daughter bubble, it can be still considered as "single bubble". In contrast, the chemically active form after slight parameter change has been identified as a permanent group of several bubbles. Fig. 2 gives several examples of such sonochemically active bubble clusters. Most of the time, the group contains a few medium sized satellite bubbles around one larger central bubble, and a greater number of small bubbles (some close to optical resolution). A permanent strong interaction between the bubbles leads to deformations, translations, merging and splitting on the time scale of one to a few acoustic cycles. Larger bubbles show faster motion than the smaller ones

which is in accordance to an interaction driven by secondary Bjerknes forces [3,19]. Bubble translation speeds in the cluster can reach the order of several m/s.

The question how exactly the chemical product emerges from the bubbles cannot clearly be answered yet. Most close-up recordings at high speed which resolve bubble dynamics do not show a sufficient contrast to resolve at the same time the product, possibly due to a concentration too low for obscuring the very bright background illumination needed for the high frame rates, compare Fig. 2(a)–(d). In some sequences, however, in particular at longer exposure times and slower recording speed, a darker trace of
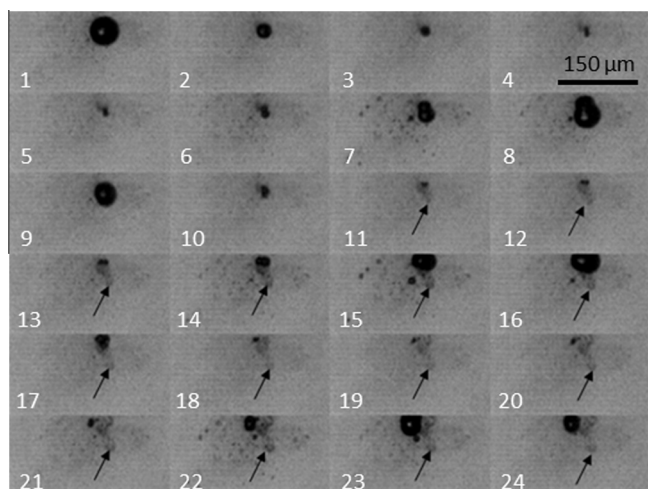
Fig. 3. Close-up sequence of a reacting cluster at 18.4 kHz (interval between frames is 7.1 ms, but actual recording is with 420,000 fps and exposure time 1 μs, i.e. only every 3000th frame is shown). Arrows mark a clear trace of chemical product which seems to be released from the large central bubble (frame width 300 μm).

product is recognisable. It can be distinguished from a cloud of tiny bubbles mainly by the lack of brightness modulation (which is characteristic for bubbles in the sound field as they undergo volume oscillations). An example of the chemical reaction output occurring as a halo around the cluster is given in Fig. 2(e). Another case is shown in Fig. 3 where the fumaric acid appears to leave the

largest bubble on the lower side. From the sequence one gets the impression that the product ejection happens intermittently: a grey blot suddenly appears in frame 11 (arrow) and then stays for a while without much change. An extension of the grey zone happens in frame 18 (at its top), and afterwards the blot seems to stay again mainly unchanged.

A comparison of high-speed sequences of a sonochemically passive single bubble and an active cluster is presented in Fig. 4(a) and (b), respectively. The quite stable single bubble in (a) is well fixed in space and oscillates in the repetitive fashion well-known from SBSL experiments. However, from time to time a surface mode appears (often $n = 2$) and deformed bubble shapes and separation of satellite bubbles are observed. The split-off bubbles are mostly rather small and re-merge immediately, and thus we keep the notion of a "single bubble" for this case. The behaviour is probably due to the only moderate degassing of the water and is very reminiscent to the "unstable SBSL" [20] where the diffusional equilibrium of the bubble is not reached and a slow growth of gas mass (over many acoustic cycles) lets the bubble run into a shape instability.

The situation changes significantly if sonochemical activity sets in, as is visible in the series Fig. 4(b). The small clusters show a high variability of bubble numbers, shapes, and positions, and almost every acoustic driving period a different picture occurs. In particular the larger bubbles experience a strong mutual interaction, but also the smaller satellites and "mist" bubbles are interacting, likewise preferentially with the larger ones. An example of a relatively fast translating satellite bubble, reaching about 6 m/s during its collapse, is indicated in frames 65 and 66. All bubbles in the cluster
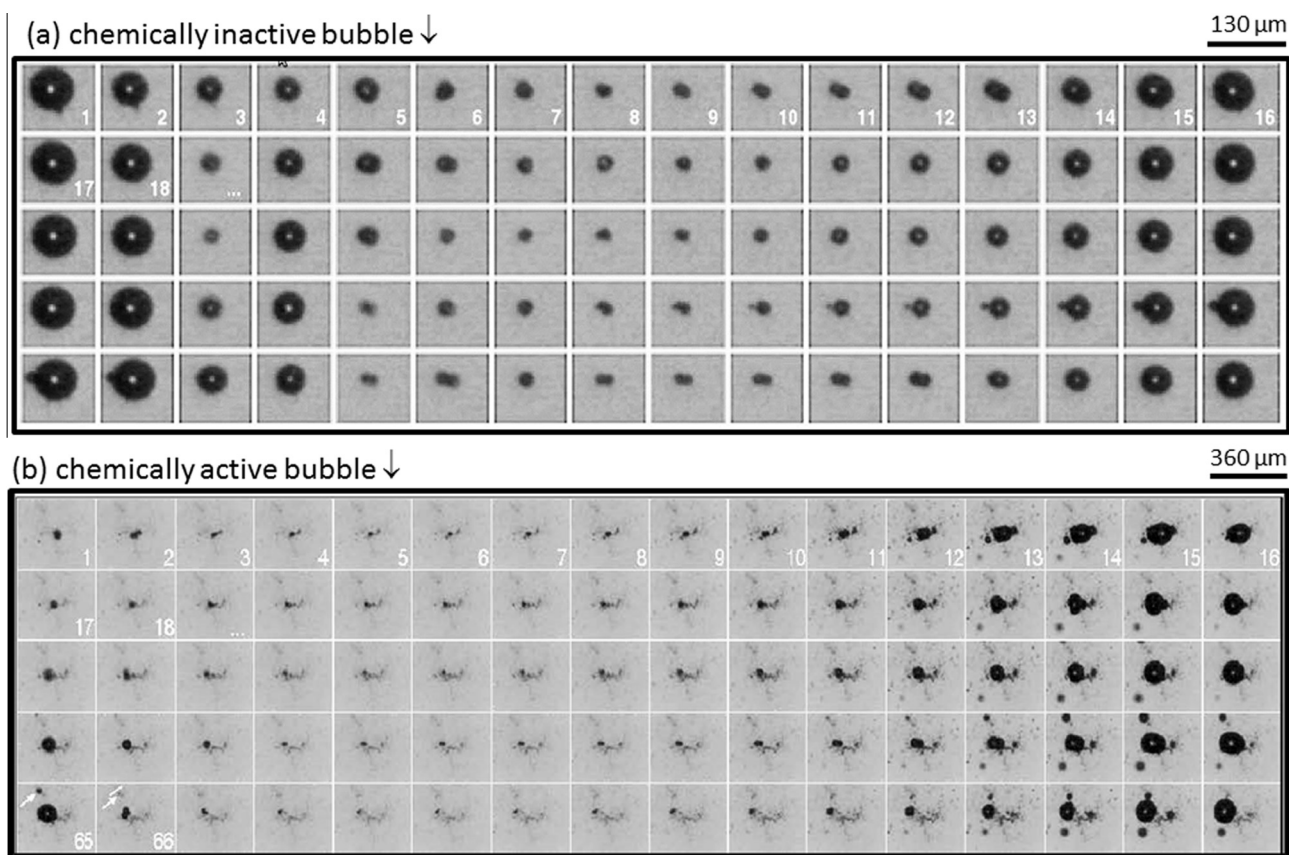
Fig. 4. (a) Sequence from a high-speed recording of a chemically inactive bubble trapped in the cell at a driving frequency of 18.55 kHz and recorded with 300,000 frames/s (3.3 μs interval between frames, 1 μs exposure time, frame width 130 μm). One period (54.3 μs) corresponds roughly to one row of 16 frames (53.3 μs). (b) Sequence from a similar recording after slight increase of the driving voltage (note the larger frame width of 360 μm). The bubble has converted into a chemically active bubble cluster, i.e., satellite bubbles surround the large central one. Arrows in frames 65 and 66 point to a satellite bubble before and after its collapse; the line in frame 66 marks the bubble position from frame 65, which indicates a jump of about 20 μm. This corresponds to a translation velocity of about 6 m/s.

follow the alternating sound pressure with volume oscillations which can be well perceived in the fast recording. The smaller bubbles collapse earlier than the larger ones, and they might partly disappear from the image due to the limited resolution (here about 5 μm).

3.2. Numerical results

From the experimental high-speed observations, quantitative data have been extracted in order to obtain more information about the active or inactive bubbles and their dynamics. Particular interest lies in the rest (or equilibrium) radius R_0 of the bubble [3]. It is a measure of "true" bubble size in terms of the amount of non-condensable gas inside, but is a quantity not straightforward to measure as the bubbles show strong volume oscillations. A second unknown of importance is the local acoustic pressure amplitude p_a which could not be measured directly. Under certain assumptions, knowledge of R_0 and p_a allows a numerical estimate of the conditions during the main bubble collapse, which is too fast and small scale to be observed directly in the experiment. For this purpose, we fit the observed radius-time data by a Keller–Miksis single bubble model [21,22] where R_0 and p_a enter as the essential parameters (for known acoustic frequency). Most severe idealisations of the model are spherical symmetry, sinusoidal acoustic driving pressure, and a homogeneous bubble interior with a van-der-Waals equation of state under isothermal expansion/compression. Although these assumptions are definitely not strictly fulfilled, in particular for reacting bubbles in a cluster, we still expect a more or less realistic estimate of minimum radius and thus compression rate during the main collapse. For more detailed estimates of bubble temperatures, pressures, and reaction yields, advanced models have to be employed.

The model equations have been adopted from Parlitz et al. [22] where the exact formulation can be found. In an optimisation procedure by visual judgement, a "best" fit of the data by variation of (R_0, p_a) has been obtained with a focus on matching the maximum radius, the collapse phase, and the afterbounce dynamics. Fig. 5 and Table 1 show the results for the two cases of an inactive single bubble (from Fig. 4(a)) and an active one. The active bubble data have been taken from the largest bubble in an active bubble cluster similar to Fig. 4(b). For enhancement of the temporal resolution, repetitive bubble oscillations have been back-projected with correct phases onto a single oscillation period. This method worked well for just a few consecutive acoustic periods because of the slow bubble growth in the inactive case and the strong bubble interaction in the active clusters. The measurement points in Fig. 5(a) and (b) are both composed from three successive cycles. While quite good agreement of expansion, collapse, and afterbounce periods could be obtained, less good fittings of first rebound height and of the transitional phase before large expansion are found. These deviations of the order of 10–20% in radius are possibly based on the approximations referred to above, and they are considered as tolerable.

From the curves of the "best fitting" values of R_0 and p_a we extracted minimum and maximum radius during one period to calculate the compression ratio R_0/R_{min} and the expansion/compression ratio R_{max}/R_{min} of the main collapse. Of course, one expects that both measures should be essentially equivalent, but due to the nonlinear nature of the bubble dynamics, this does not necessarily have to be the case. Indeed, the surprising finding is here that the compression ratios of active and passive bubbles are quite similar, while the expansion/compression ratios differ considerably, see Table 1. A closer consideration shows that the former is a good indicator for the largest pressures and temperatures in the collapse (as it measures the compression of the non-condensable gas mass), while the latter is also suited to judge about the bubble stability (since it measures the total available energy which needs not to go completely in gas compression). The much higher R_{max}/R_{min} of
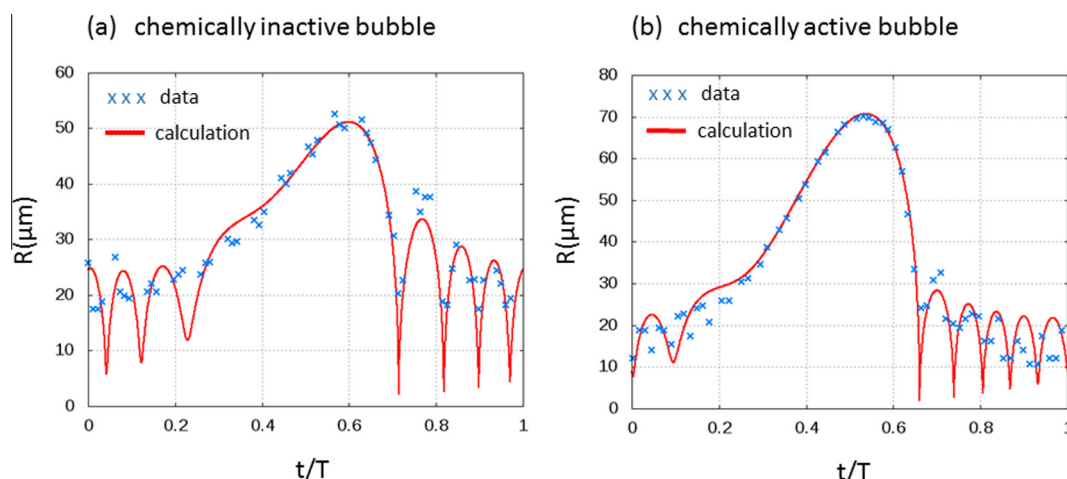
Fig. 5. Comparison of experimental radius-time data and a fitted numerical spherical bubble model at $f = 18{,}550$ Hz acoustic driving frequency. Observed radius values have been obtained automatically after image processing (contrast enhancement, threshold discrimination, automatic pixel diameter) using ImageJ [23]. The values of three subsequent bubble oscillations have been back-projected with correct phases onto a single oscillation period $T = 1/f = 53.9$ μs. (a) Inactive single bubble from Fig. 4(a); fit parameters are $p_a = 105.5$ kPa, $R_0 = 18.25$ μm. (b) Largest bubble of an active bubble cluster similar to Fig. 4(b), but recorded at 420,000 fps; fit parameters are $p_a = 123.0$ kPa, $R_0 = 17.15$ μm. For resulting compression ratios see Table 1.

Table 1
Comparison of parameters p_a and R_0 and resulting maximum/minimum radii and compression ratios of the fit for a sonochemically inactive single bubble (first row) and a sonochemically active bubble (largest from a cluster; second row).

	Frequency [Hz]	ac. press. ampl. p_a [kPa]	Rest radius R_0 [μm]	Max. radius R_{max} [μm]	Min. radius R_{min} [μm]	R_0/R_{min}	R_{max}/R_{min}
Inactive bubble	18,550	105.5	18.25	51.14	2.24	8.13	22.78
Active bubble	18,550	123.0	17.15	70.68	2.03	8.45	34.85

the active bubble (which is driven stronger) seems not to be converted into much higher temperatures, but the faster imploding bubble wall supports shape instability. A very cautious interpretation would be that this is another indication that the non-spherical dynamics of an active (cluster) bubble is contributing to the chemistry after the transition from a passive (single) bubble (triggered by acoustic pressure increase), and not "just" a higher temperature and pressure inside the collapsing bubble. Of course, our data for such a conclusion are sparse, and the results need confirmation by a more extensive evaluation of observations, preferably with an advanced bubble model. In any case, to our knowledge, the experimental and fitted data given in Fig. 5 and Table 1 constitute the first well resolved dynamics of individual bubbles for a transition from quiet to sonochemically active.

4. Discussion

Our results confirm the findings from previous work which was partly summarised in the introduction: efficient liquid phase sonochemistry seems to require not only sufficiently strong collapse compression and heating of the bubble interior, but as well some disturbance of the spherical symmetry of bubble dynamics. In our case we observe a clear correlation of chemical reaction (in terms of the bromine radical mediated isomerization reaction of maleic to fumaric acid) with occurrence of a small bubble cluster instead of a single bubble. It was not possible to produce a visible reaction product from a stable single bubble, nor from slightly diffusionally unstable and sometimes splitting single bubbles like that shown in Fig. 4(a). Our interpretation is that maleic acid, which should be present in the bubble interior only to a negligible amount due to its very low vapour pressure, is efficiently mixed inside only in the cluster environment. Dibromomethane, on the other hand, might react in the gas phase, but bromine radicals then have to be transported out of the bubble into the liquid. Thus we suppose that a certain mixture of liquid and bubble interior is beneficial (if not necessary) for the full reaction to occur, and that this is not taking place for the single bubble.[1]

From fitting radius-time data of an inactive (single) bubble and an active bubble (largest one in a cluster) by a numerical model, we observed roughly similar compression ratios R_0/R_{min} for both cases, but considerable higher expansion/compression ratio R_{max}/R_{min} of the active bubble. We tend to interpret this finding such that the heating of the observed single bubble is in principle sufficient for the desired reaction, but that a bubble cluster environment is needed for realising it. Again, the (otherwise missing) mixture of liquid and gas phase in the bubble appears to be the reason. The transition to the bubble cluster (and active chemistry) is reached for higher driving pressures and happens via shape instability and splitting of the main bubble.

We cannot rule out completely a coincident correlation of both the chemical reaction threshold and the spherical stability threshold of the bubble in our set-up. In particular, the dissolved gas content (which determines diffusional bubble growth and stability) could not be sufficiently well controlled in our experiment, and

one might expect higher compression ratios of non-splitting single bubbles at stronger and sustained degassing of the liquid. However, within the explored parameter space of driving pressure, acoustic frequency, and dissolved air content above about 25%, a reacting single bubble was never encountered. In other, only preliminary experiments, sonoluminescence of the bubbles was additionally monitored. There, at strong degassing and for increasing the driving pressure, the transition of a chemical active cluster to a single SBSL bubble was realised (but in a very transitory modality), and the appearance of solid product seemed to stop immediately with occurrence of SBSL. This observation further supports our conclusion above, but the transition "cluster to SBSL" could not be investigated closer in the experiments reported here.

The connection of liquid phase sonochemistry and non-spherical bubble dynamics has been highlighted also in other types of reactions. Sonoluminescence emissions of excited alkali metals from dissolved salts in water or acids are as well interpreted as a signature of liquid–gas mixture in the collapsing bubble, as the metal ions are non-volatile [24–26,4,27,28]. In some works a correlation of bubble translational motion and emission lines like Na* has been observed, which can as well be interpreted as a source of non-spherical dynamics. In particular a forward jetting collapse of a sufficiently fast moving bubble has been predicted [12,13] and observed [29], and the jetting seems to be an appropriate collapse modality of bubbles in sulphuric acid to emit the Na* line [30]. The jetting mechanism as a source of liquid micro-drop injection into the hot gas phase has also been proposed by Troia et al. for the CCl$_4$ decomposition in the Weissler type reaction [10], even though for a single levitated bubble. Recently, hints have been found that few-bubble cluster dynamics can boost emission of metal lines in aqueous solutions of the corresponding salts [27,31]. Possible mechanisms of the liquid–gas mixture apart from jetting are surface shape (modal) oscillations [26], bubble splitting, and bubble coalescence. All these mechanisms might be contributing in the chemically active few-bubble clusters we observe, but discrimination between the different scenarios is not yet possible. Some subjective visual impressions from high-speed movies tend to the opinion that surface modes are a main agent, and that mainly or only the largest cluster bubble is really active.

We have to note that our use of the term "chemically (in)active" might be misleading in the sense that we are not referring to any chemistry in the bubble. Reactions might run in the single and possibly perfectly spherical bubble as well, as long as the gas and vapour phase and a thin liquid shell are affected. For instance, (water) vapour decomposition and reactions of air will occur if sufficient collapse compression of the bubble takes place, irrespective of liquid/gas mixing. This might explain the observations by Didenko and Suslick [15] for SBSL bubbles in water. On the other hand, an effective transfer of products from gas/vapour chemistry into the liquid will also be supported by some mixture mechanism. From this point of view, the measurements by Koda et al. [16] would fit as they claim a higher efficiency of (observed products of) reactions of air and water vapour (HNO$_2$ and HNO$_3$). For reactions with a contributing liquid phase, gas/liquid mixture processes induced by bubble dynamics can clearly support the efficiency by supplying reagent into and transporting products out of the bubble. In our reported case above, this support appears to be essential. It might of course, depending on the detailed conditions, be "paid for" by somehow lower reaction temperatures and pressures due to less focussing collapse geometries and energy lost for heating of the liquid micro drops.

Acknowledgements

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[1] In a side remark, we like to note that the cause of the directed emission of product from the reaction site in form of a streak remains unclear. The distribution of solid fumaric acid within the reacting cluster can appear localised close to a bubble (Fig. 3) or as a "halo", i.e., an outward diffusing cloud (Fig. 2(e)). Still, on a macroscopic scale, the product flows in a clear direction away from the bubbles (which can, however, change on longer time scales). Apparently, the bubble cluster is generating a form of dipole flow in the cuvette, irrespective of its internal violent "micro" turbulence associated with the close multi-bubble oscillations and motions. Potentially, a preferential direction of an $n = 2$ surface mode of the largest bubble and its splitting/merging might contribute and works as an "extension" of Longuet-Higgins' mechanism [11,14], which was formulated for a single levitated bubble performing oscillatory translation or jetting.

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