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Impact of bubble coalescence in the determination of cavitation bubble sizes using a pulsed US technique

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Introduction

Important to estimate reliably the bubble sizes, in particular the **distribution of bubble ambient radii** (i.e., bubble radii at zero acoustic pressure) R_0

necessary for every modelling of bubble behavior

But: **bubble sizes are far from being monodisperse**

- bubbles too small to be active
- too big bubbles resulting from coalescence of smaller ones
- of interest for sonochemistry: only cavitation bubbles

Direct experimental determinations

acoustic scattering: Niederdrank & Wiesand, 37 kHz: majority of radii 4-10 µm

laser diffraction and **phase Doppler**: Burdin et al.: 20 kHz, majority of radii 4-10 µm

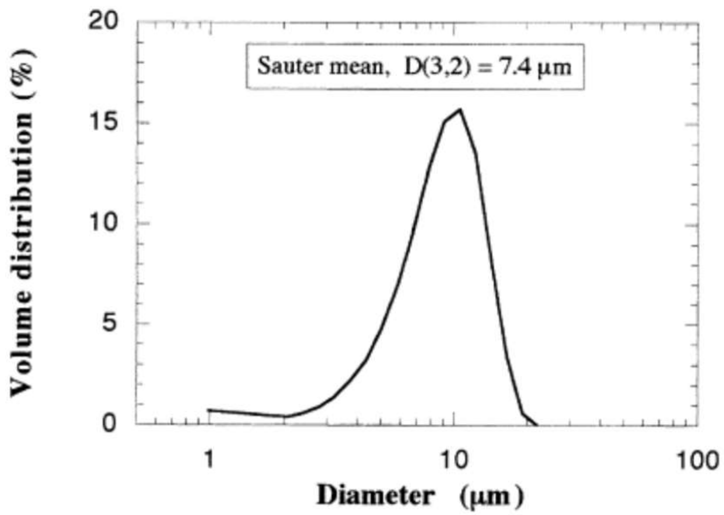


Fig. 6. Volume distribution of bubble cloud measured by the LD instrument.

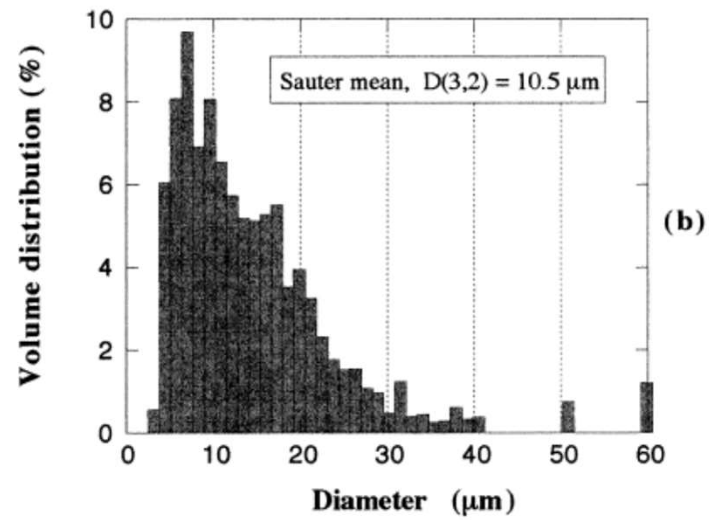


Fig. 7. Velocity (a) and size (b) distributions (number and volume distributions respectively) of bubble cloud measured using the PD instrument.

All bubbles measured

T. Niederdrank, B. Wiesand, The temperature dependent behaviour of a cavitation bubble field, Acustica, 84 (1998) 425-431.

F. Burdin, N.A. Tsochatzidis, P. Guiraud, A.M. Wilhelm, H. Delmas, Characterisation of the acoustic cavitation cloud by two laser techniques, Ultrasonics Sonochemistry, 6 (1999) 43-51.

Direct experimental determinations: imaging

Method initially based on a **direct high-speed imaging of all visible bubbles**

Measurement of the bubble size distribution in a streamer structure at 20 kHz (**standing wave**)

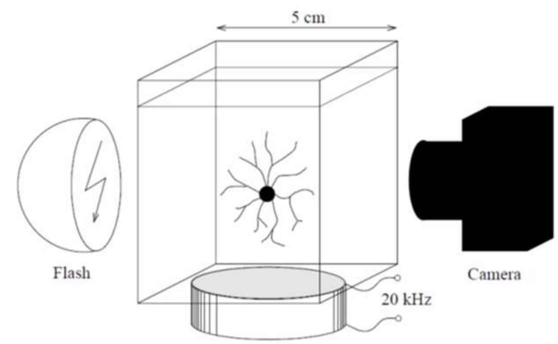
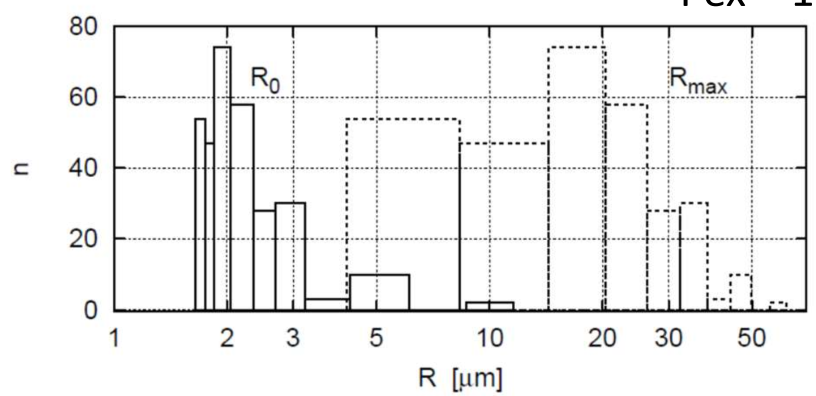


Figure 1: Schematic setup of the cavitation experiment: A piezoceramic disc transducer induces streamers in a rectangular PMMA cell filled with tap water. A microsecond flashlight illuminates the picture recorded by a computer controlled camera

Most imaged bubbles have R_{max} 5-40 µm (R=5 µm corresponds to limit of detection)

Recalculation of the bubble equilibrium radii leads to values in the range of a few µm.

Pex = 130 kPa



'the important bubbles in sonochemistry range around a micrometer in size'

R. Mettin, S. Luther, W. Lauterborn, Bubble size distribution and structures in acoustic cavitation, in: 2nd Conf. on Applications of Power Ultrasound in Physical and Chemical Processing, 1999, pp. 125-129.

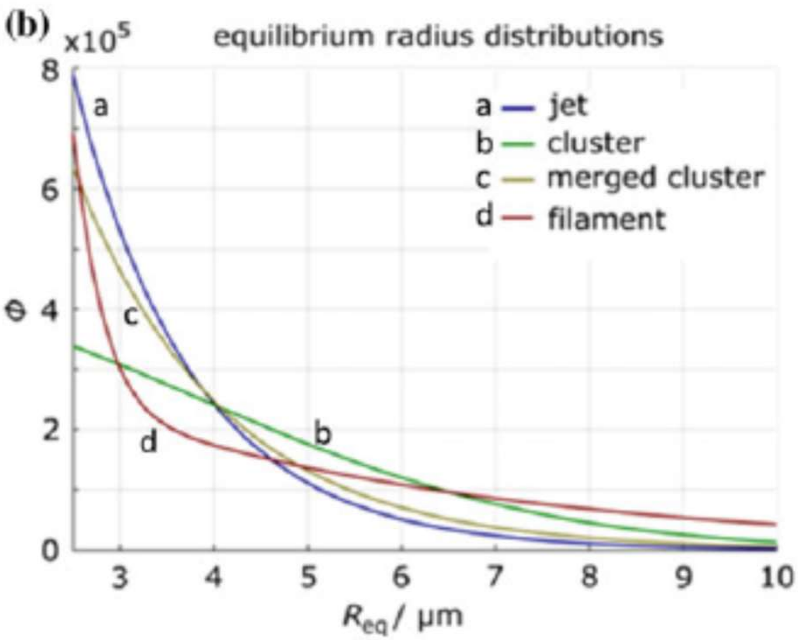
Direct experimental determinations: imaging

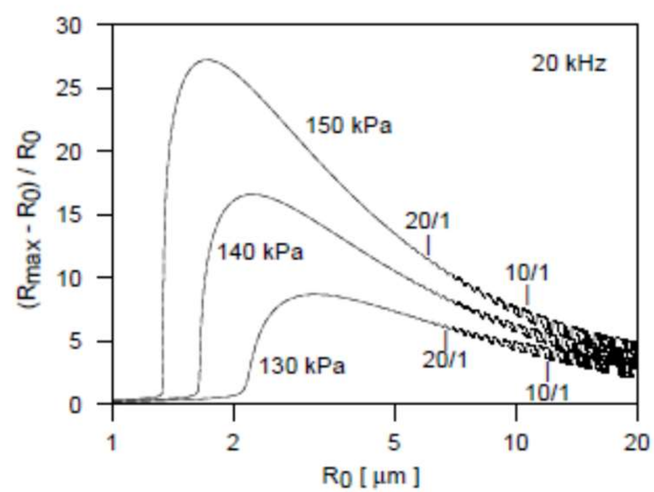
Method further developed by coupling it to a statistical approach → no need for a standing wave, lower detection limit, access to $R_0 \geq 2.2$ µm.
(27.5 kHz, air, 20°C)

No bubble observed with R>60µm due to shape instabilities

R_0 mostly in the range 2-4 µm
(possibly below 2 µm also)

in agreement with calculated bubble sizes





F. Reuter, S. Lesnik, K. Ayaz-Bustami, G. Brenner, R. Mettin, Ultrasonics Sonochemistry, 55 (2019) 383-394.

W. Lauterborn, R. Mettin, 'Nonlinear bubble dynamics: response curves and more', in Sonochemistry and Sonoluminescence, ed. by L.A. Crum, T.J. Mason, J.L. Reisse, K.S. Suslick (Kluwer Academic Publishers, Dordrecht, 1999)

Limitations of direct methods

Reliable largely validated methods

However

- **limited to low frequencies** due to technical limitations (f ↑: R ↓, period ↓).

  For instance, Reuter et al. indicated that due to the **optical resolution**, only bubbles larger than **10.5 µm** are accessible to the measurement, or equilibrium radii larger than 2.2 µm with their statistical approach.

- in most cases (except Cairos et al.), direct observations focus on **all present bubbles**, not just on cavitation bubbles, which explains the reported large size intervals.

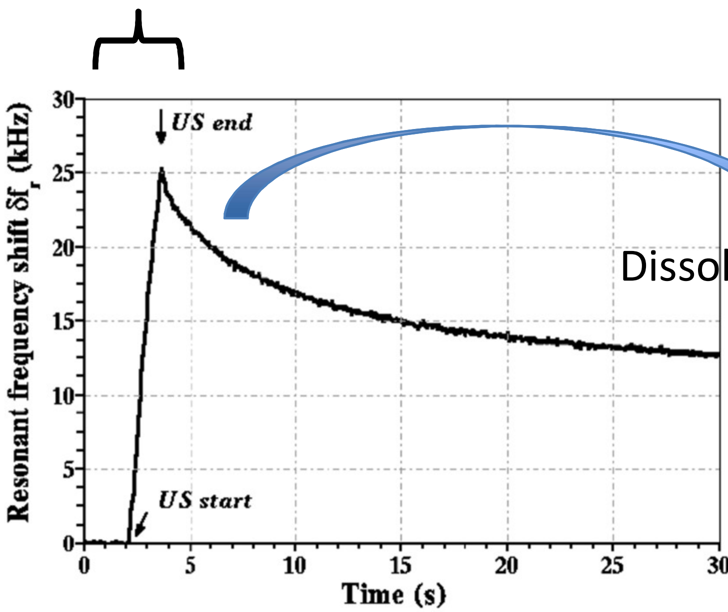
F. Reuter et al., Ultrason. Sonochem., 55 (2019) 383-394

C. Cairos, R. Mettin, Simultaneous High-Speed Recording of Sonoluminescence and Bubble Dynamics in Multibubble Fields, Phys. Rev. Lett., 118 (2017)

Indirect methods

All based on the ***monitoring of bubble dissolution after US irradiation***

US irradiation during a given time:
development of a bubble population



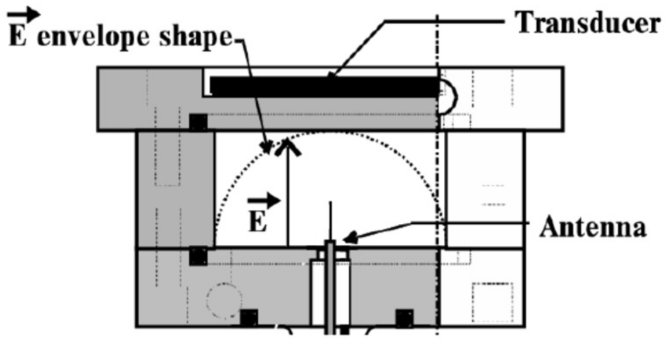
Dissolution kinetics

Bubble size distribution

Method & its resolution determine the size range accessible to the experiment

Indirect methods

Measurement of the **void rate** (total volume of bubbles) **after the end of the US irradiation** using an **electromagnetic method**



air-saturated water
300 & 1100 kHz

Reactor = electromagnetic resonant cavity, driven at resonance by a wire antenna (f_r close to 390 MHz)

Emergence of cavitation bubbles: global water permittivity ↓ and resonant frequency f_r ↑

Void rate proportional to the resonant frequency shift δf_r

At 344 kHz most bubbles had $R_0 <$ 3.5 µm

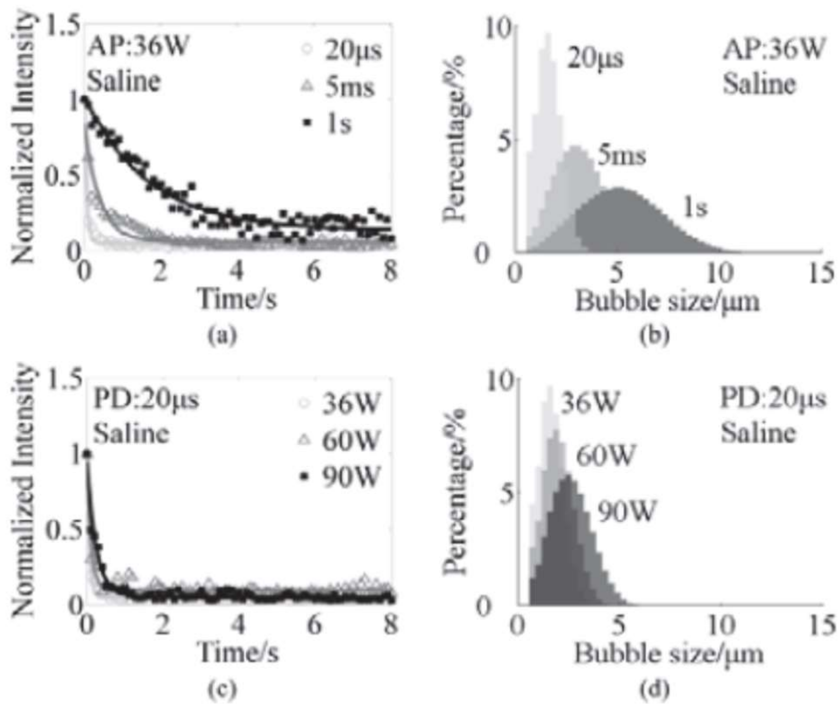
It was shown that *if the US irradiation is too long, coalescence of bubbles can perturb the measurement and lead to a shift of the determined bubble size distribution towards bigger sizes*

S. Labouret, J. Frohly, Europ. Phys. J.-Appl. Phys., 10 (2000) 231- 237; S. Labouret, J. Frohly, Europ. Phys. J.-Appl. Phys., 19 (2002) 39-54; S. Labouret, J. Frohly, in: Int. Congress on Ultrasonics, Vienna, 2007; S. Labouret, J. Frohly, in: 10ème Congrès Français d'Acoustique, Lyon, France, 2010.

Indirect methods

Scattering intensity of bubbles vs. time followed with an **acoustic method**.

HIFU 1.2 or 5 MHz
Air-saturated saline



It demonstrated the feasibility of measurement of bubble size distributions at frequencies as high as 5 MHz in a focused configuration.

'Larger bubbles were induced by longer pulses'

S.S. Xu, Y.J. Zong, X.D. Liu, M.X. Wan, Size Distribution Estimation of Cavitation Bubble Cloud via Bubbles Dissolution Using an Ultrasound Wide-Beam Method, in: J.B. Fowlkes, V.A. Salgaonkar (Eds.) Proceedings from the 14th International Symposium on Therapeutic Ultrasound, Amer Inst Physics, Melville, 2017.

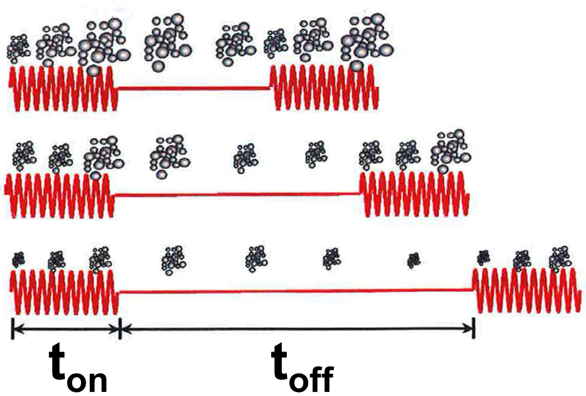
Indirect methods

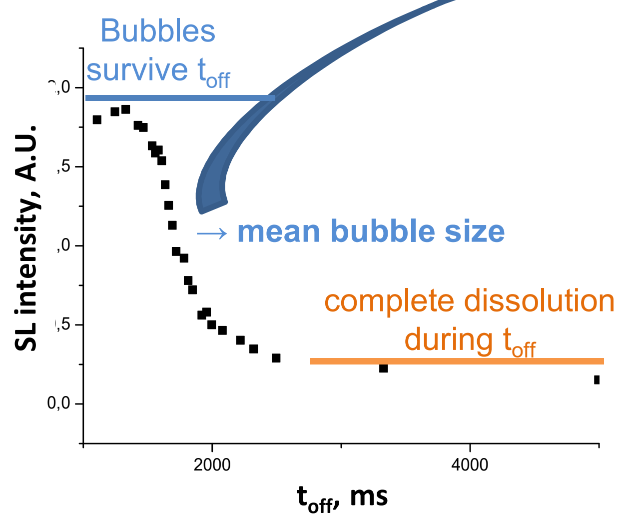
Monitoring technique = **measurement of emitted light (SCL or SL) intensity**.
Advantage: *restricts the population of studied bubbles to (SCL or SL) active bubbles*.

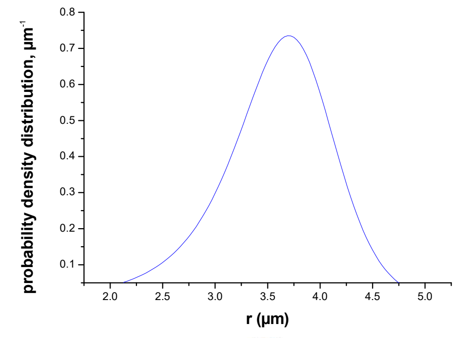
US during a constant on-time (t_{on}): formation of a certain active bubble population

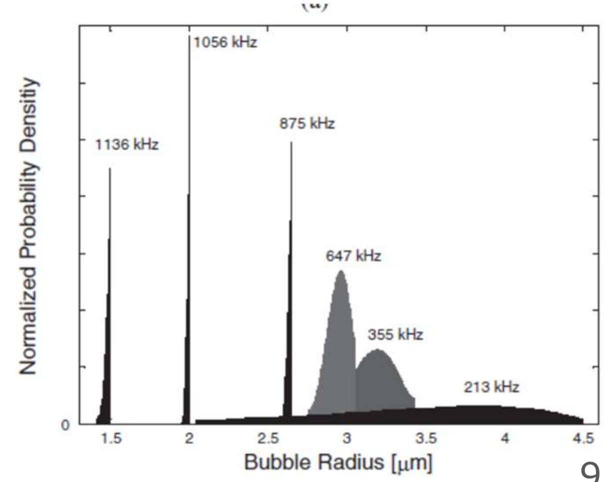
In the following off-time (t_{off}), no US, bubbles are allowed to dissolve

Variation of t_{off} in a large interval to determine the time needed for bubbles to completely dissolve









Lee, Ashokkumar, Kentish, Grieser, J. Am. Chem. Soc. 127 (2005) 16810-16811
Brotchie, Grieser, Ashokkumar, Phys. Rev. Lett. 102(8) (2009)

Further validation needed

US **on-time arbitrarily fixed** at 4 or 6 ms

In light of the observations by Labouret and Frohly with their electromagnetic technique or by Xu et al. under high intensity focused US (HIFU, 1.2 MHz and 5 MHz), ***there may be coalescence***

Lee et al.: 515 kHz

- air-saturated water: size distribution of 2.8-3.7 µm
- aqueous 1.5 mM SDS: 0.9-1.7 µm

smaller size range

SDS known to limit bubble coalescence: maybe coalesced bubbles were measured in water

→ necessary to further investigate possible phenomena taking place under pulsed US

J. Lee, M. Ashokkumar, S. Kentish, F. Grieser, J. Am. Chem. Soc., 127 (2005) 16810-16811

Further validation needed

Study (at 362 kHz):

- impact of **pulse on-time** on bubble size distribution (0.5 - 8 ms, Ar)
- effect of a **continuous Ar gas flow**, in line with the recent observation of different bubble sizes in NaCl solutions pre-saturated with He or Ar or continuously sparged with these gases

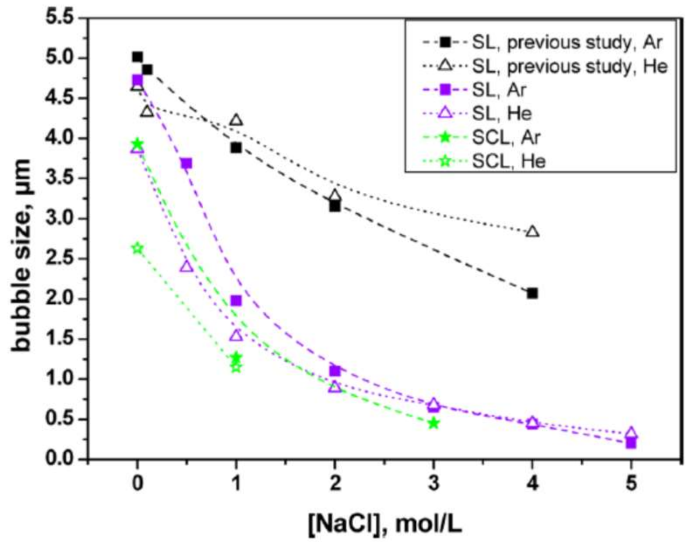


Figure 5. Evolution of the average SL (respectively SCL) bubble size with NaCl concentration, under Ar and He, at 355 kHz under continuous gas bubbling (present data) and at 515 kHz after saturation of the solution with the chosen gas.[4]

Saturation → continuous gas flow: strong decrase in bubble size (NaCl solutions)

- effects of **acoustic power** and possible **formation of a standing-wave**
- gases other than Ar

R. Pflieger, J. Lee, S.I. Nikitenko, M. Ashokkumar, Journal of Physical Chemistry B, 119 (2015) 12682-12688

Impact of pulse on-time

Ar sat., 362 kHz, 10°C, PMT placed on the side of the reactor

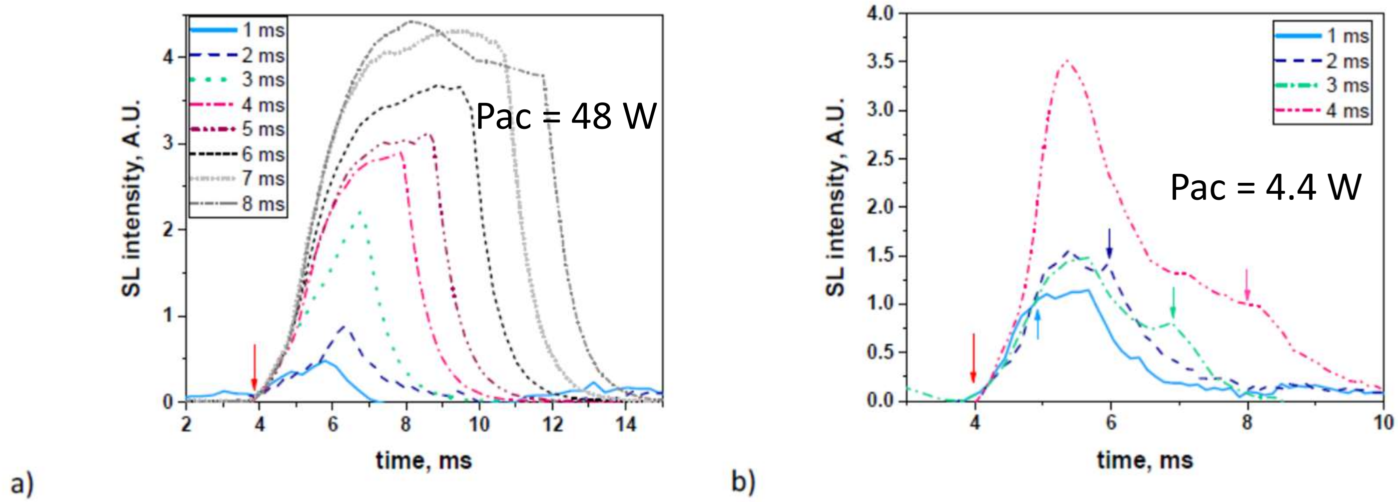


Fig. 1: Evolution of the SL intensity during t_{on}, for various t_{on} values, Ar-saturated water, 362 kHz, 10°C, a) P_{ac} = 48 W, (V_{PMT} = 600 V for 3-8 ms, 1000 V for 1-2 ms), b) P_{ac} = 4.4 W (V_{PMT} = 1000 V) (curves obtained at higher t_{on} are presented in Fig. 2SI in Supporting Information) (for each curve, the second arrow indicates the end of the US pulse).

t_{on} = 1-3 ms, the SL intensity steadily increases: **initial increase in the number of active bubbles**

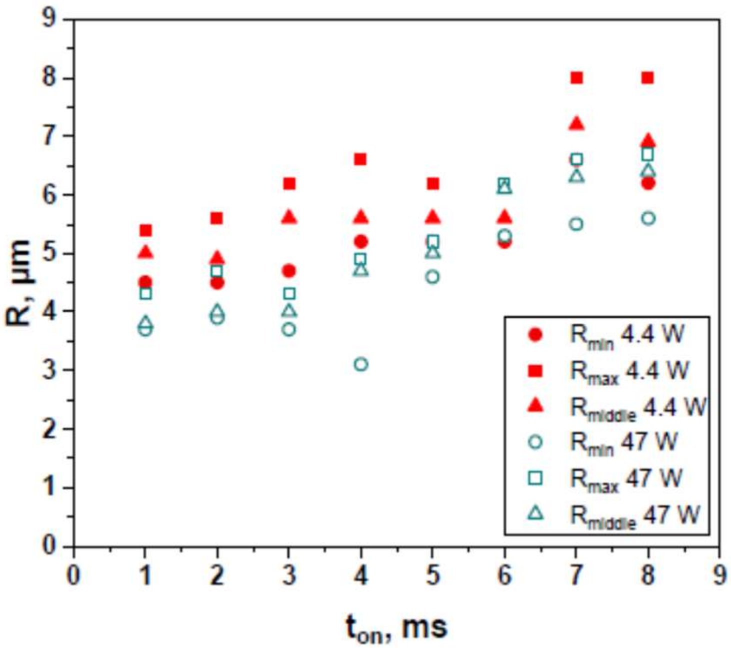
t_{on} = 4-6 ms the SL intensity then reaches a plateau: **apparent steady-state** bubble population

For longer on-times, plateau followed by a decrease in intensity: **interactions** between bubbles **decrease the number of active bubbles**

Previous works chose an on-time (4-6 ms) corresponding to a reached steady-state population (and high SL intensity).

M. Ashokkumar, R. Hall, P. Mulvaney, F. Grieser, J. Phys. Chem. B 101 (1997) 10845–10850.
R. Pflieger, J. Bertolo, L. Gravier, S.I. Nikitenko, M. Ashokkumar, *Ultrason. Sonochem.*, 2021, 73, 105532

Impact of pulse on-time



Obtained values strongly depend on the on-time.
Mean radius at 47 W

for t_{on} = 1–3 ms: 3.8–4.0 µm
for t_{on} = 4–5 ms: 5.0–5.2 µm
for t_{on} = 6–8 ms: 6.2–6.8 µm

Longer the t_{on}, more time is available for bubbles to interact and possibly coalesce during t_{on}
What is then monitored is the dissolution of these coalesced bubbles.

e.g. for R_0 = 3.8 µm
After coalescence of 2 bubbles: $R_2 = 3.8 \sqrt[3]{2} = 4.8$ µm
3 bubbles: $R_3 = 3.8 \sqrt[3]{3} = 5.5$ µm
4 bubbles: $R_4 = 3.8 \sqrt[3]{4} = 6.0$ µm etc.

Bigger bubble sizes at lower P_{ac}! More coalescence due to standing wave

R. Pflieger, J. Bertolo, L. Gravier, S.I. Nikitenko, M. Ashokkumar, *Ultrason. Sonochem.*, 2021, 73, 105532

Limiting coalescence with SDS

Sunartio et al.: minimum coalescence for 1-2 mM SDS (air-saturated water, 358 kHz)

Bubble sizes determined for Ar-saturated water and SDS 1.5 mM solution sonicated at 362 kHz in a free surface configuration for P_{ac} = 6 & 37 W. (The SL intensity was too low at P_{ac} = 37 W and t_{on} = 0.5 ms.).

		t_{on} = 1 ms	t_{on} = 0.5 ms
P_{ac} = 37 W	H_2O	3.8–4.0 μm	–
	SDS	3.1 μm	3.0 μm
		3.4 μm	3.8 μm
		4.0 μm	
P_{ac} = 6 W	H_2O	4.0 μm	4.0 μm
			3.4 μm
	SDS	4.0 μm	4.1 μm
		3.4 μm	3.7 μm
		3.2 μm	3.0 μm

In the presence of SDS, a size **around 3.0 μm** is obtained in all cases, for both acoustic powers and t_{on} = 0.5 & 1 ms

Some coalescence still happens with SDS and the dissolution of bigger (coalesced) bubbles is observed

Considering **R_0 = 3.0 μm**, the other values can be derived from bubble coalescence:

- coalescence of 2 3.0 μm bubbles → 3.0 x $\sqrt[3]{2}$ = 3.8 μm
- Coalescence of 3 bubbles → 3.0 x $\sqrt[3]{3}$ = 4.3 μm.

D. Sunartio, M. Ashokkumar, F. Grieser, Study of the coalescence of acoustic bubbles as a function of frequency, power, and water-soluble additives, Journal of the American Chemical Society, 129 (2007) 6031-6036.

Effect of a continuous Ar gas flow

Experimental conditions chosen to limit coalescence

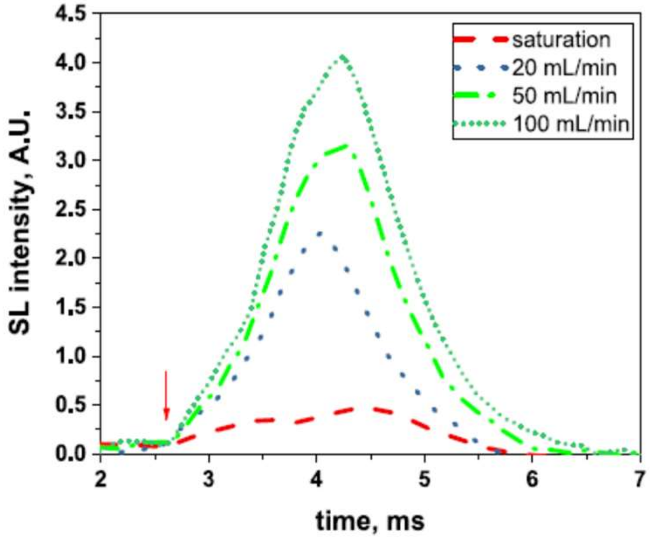


Fig. 4. Evolution of the SL intensity in water during t_{on} for different Ar gas flow rates, t_{on} = 1 ms, P_{ac} = 47 W, V_{PMT} = 1000 V, t_{off} corresponding to the SL plateau; the red arrow indicates the beginning of the US pulse. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The reached SL intensity during t_{on} increases with the gas flow rate, indicating an increasing number of SL bubbles:

- higher number of cavitation nuclei
- more pronounced coalescence (growing bubbles to their active size)

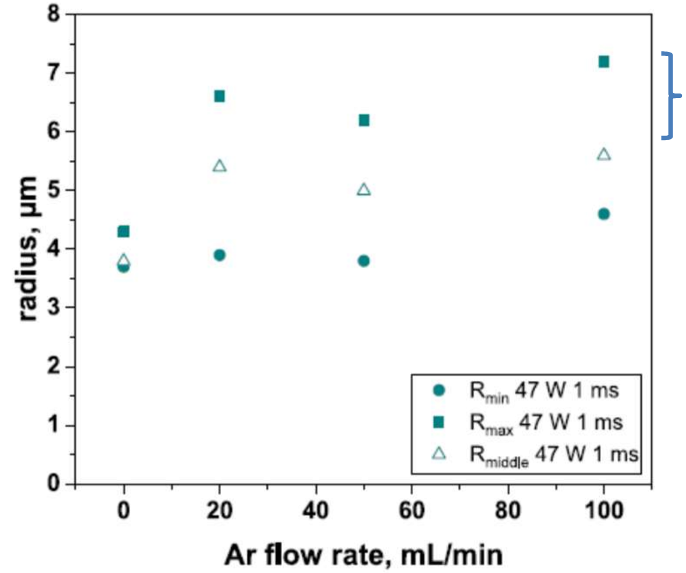


Fig. 5. Bubble sizes vs. Ar flow rate in water; t_{on} = 1 ms, 362 kHz, 10 °C, P_{ac} = 47 W.

The presence of a gas flow clearly **increases the determined bubble sizes**

Coalescence induced by the gas flow (during t_{on} and t_{off})

How to measure R_0?

Coalescence of bubbles is observed under pulsed US, both during the pulse off- and on-times.

To measure the ambient radius, take great care to avoid (minimize) coalescence

- Choose t_{on} as small as possible (≤ 1 ms for Ar)
- Avoid standing wave
- PMT focusing on a zone of lower bubble density
- No gas flow
- Check with SDS

In right conditions, measurement of the natural active bubble size can be achieved.
→ **$R_0 \approx$ 2.9-3.0 μm** for **Ar**-saturated **water** sonicated at **362 kHz**.

Considering this R_0 value and coalescence, literature values obtained with this technique can be explained.

Brotchie, Statham, Zhou, Dharmarathne, Grieser, Ashokkumar, Langmuir, 26 (2010) 12690-12695.
Pflieger, Lee, Nikitenko, Ashokkumar, J. Phys. Chem. B, 119 (2015) 12682-12688.

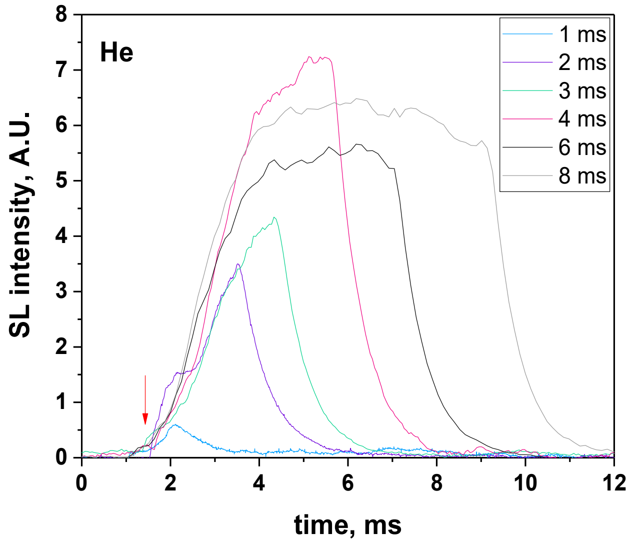
Other gases

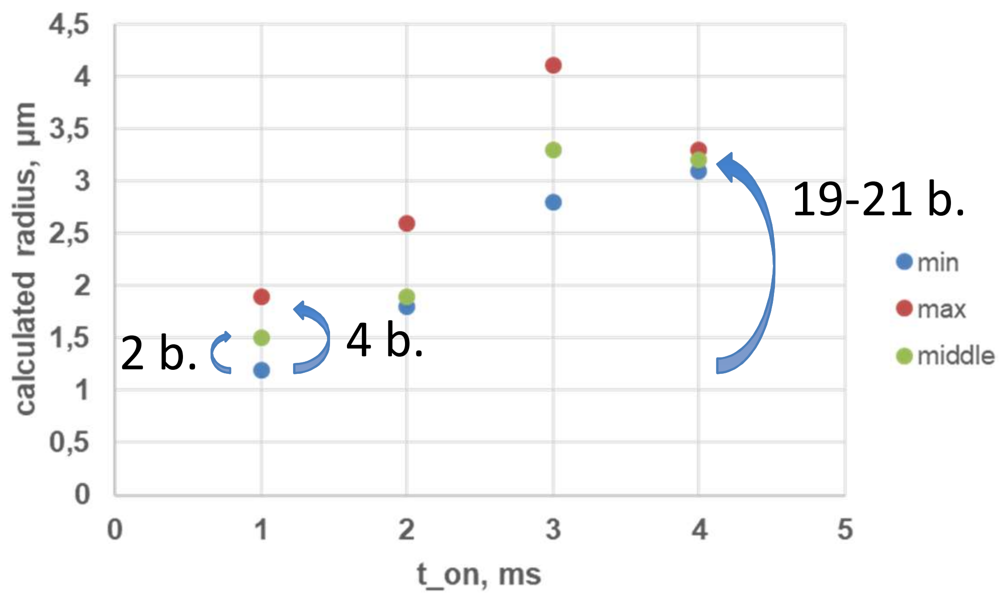
Other rare gases, showing very different solubilities: He, Xe

Polyatomic gases: O_2, N_2, air

Impact of bubble coalescence in the determination of bubble sizes using a pulsed US technique: Part 2 – Effect of the nature of saturating gas, R. Pflieger, G. Audiger, S.I. Nikitenko, M. Ashokkumar, *Ultrason. Sonochem.*, 2021, 73, 105537

He





t_{on} = 1 ms, continuous increase of the SL intensity during 1 ms
→ no indication of pronounced coalescence. R_{min} taken as **R_0 = 1.2 µm** → *close to the Blake threshold* (1 µm for p_a = 1.5 bar, 0.5 µm at 3 bar)

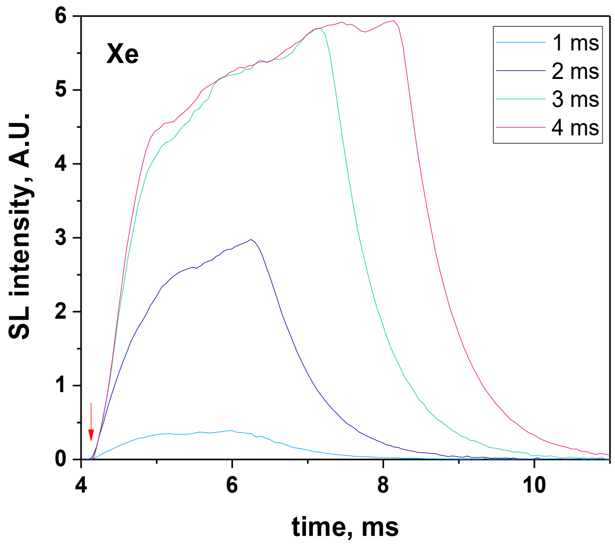
t_{on} = 2 ms: a first plateau is reached after 1 ms US
→ bubble sizes determined for t_{on} ≥ 2 ms are expected to include sizes of coalesced bubbles

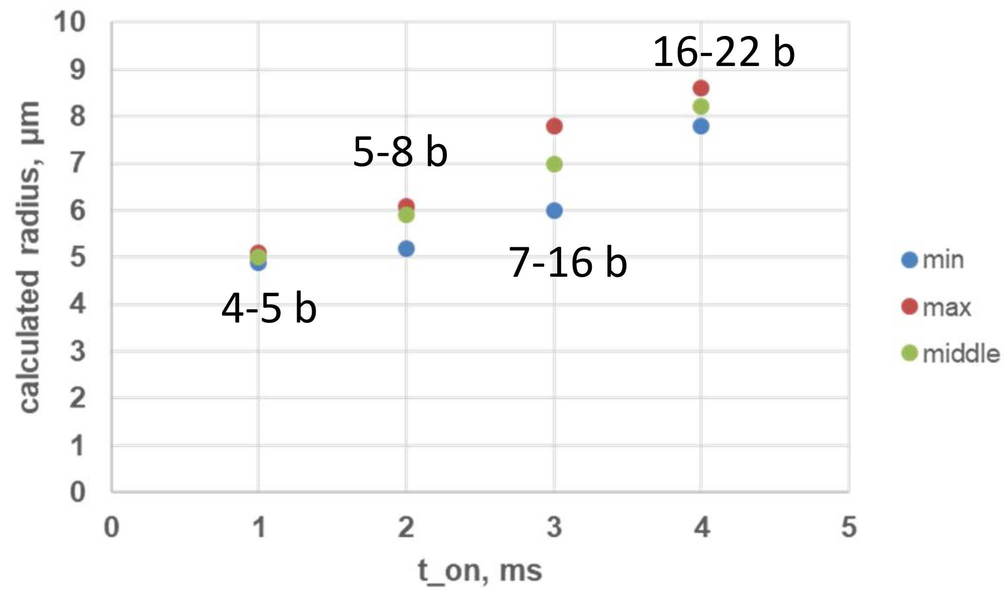
Previous literature values obtained with the same technique can be retrieved considering this R_0 and coalescence during larger t_{on}:

t_{on} = 5.8 ms, 515 kHz, He-pre-saturated water: 4.1 µm
t_{on} = 4 ms, 355 kHz, continuous gas flow: 3.75-4.0 µm

Brotchie, Statham, Zhou, Dharmarathne, Grieser, Ashokkumar, Langmuir, 26 (2010) 12690-12695.
Pflieger, Lee, Nikitenko, Ashokkumar, J. Phys. Chem. B, 119 (2015) 12682-12688.

Xe





strong bubble interactions already detected for t_{on} = 1 ms

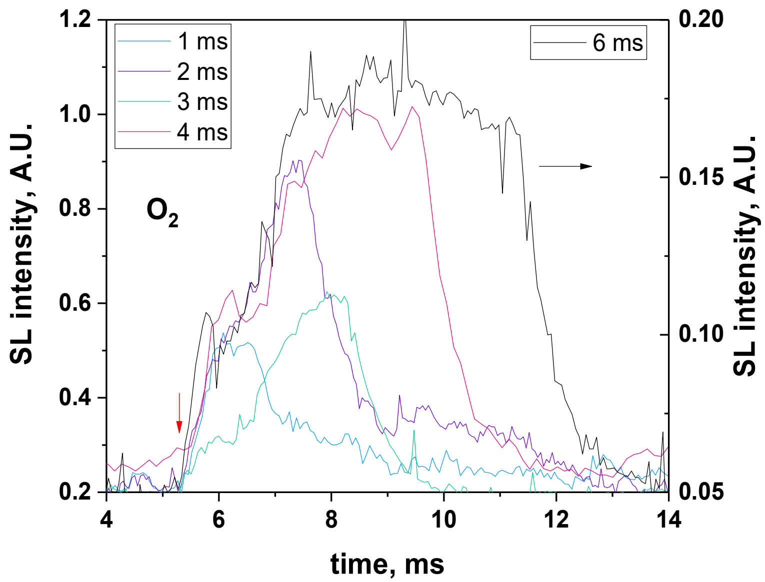
$\rightarrow$ inferred sizes include coalesced bubbles

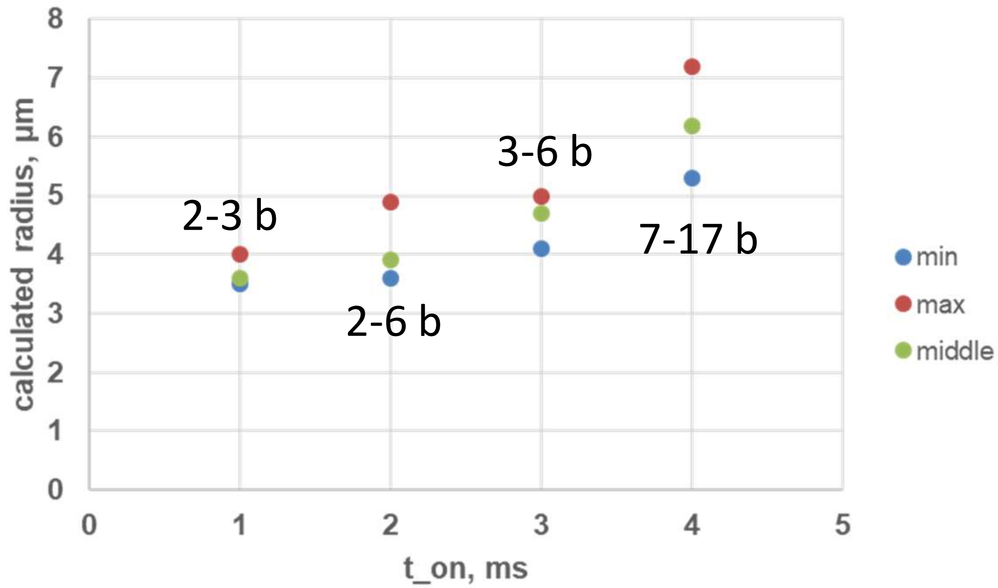
The smallest measured size (4.9 µm) may arise from the coalescence of:

- 2 bubbles, leading to a R_0 of $4.9 / \sqrt[3]{2} = 3.9$ µm
- 3 bubbles, leading to a R_0 of $4.9 / \sqrt[3]{3} = 3.4$ µm
- 4 bubbles, leading to a R_0 of $4.9 / \sqrt[3]{4} = 3.1$ µm

The values of bubble sizes obtained for the different t_{on} are best explained with **R_0 3.1 µm**.

O_2



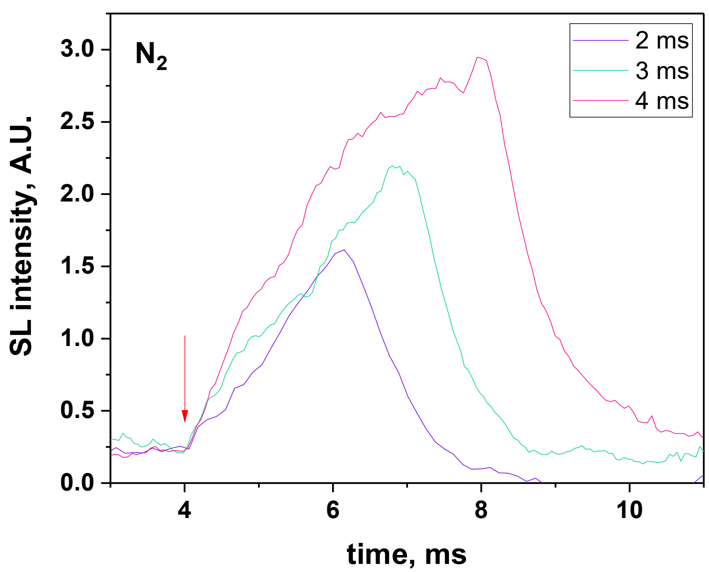


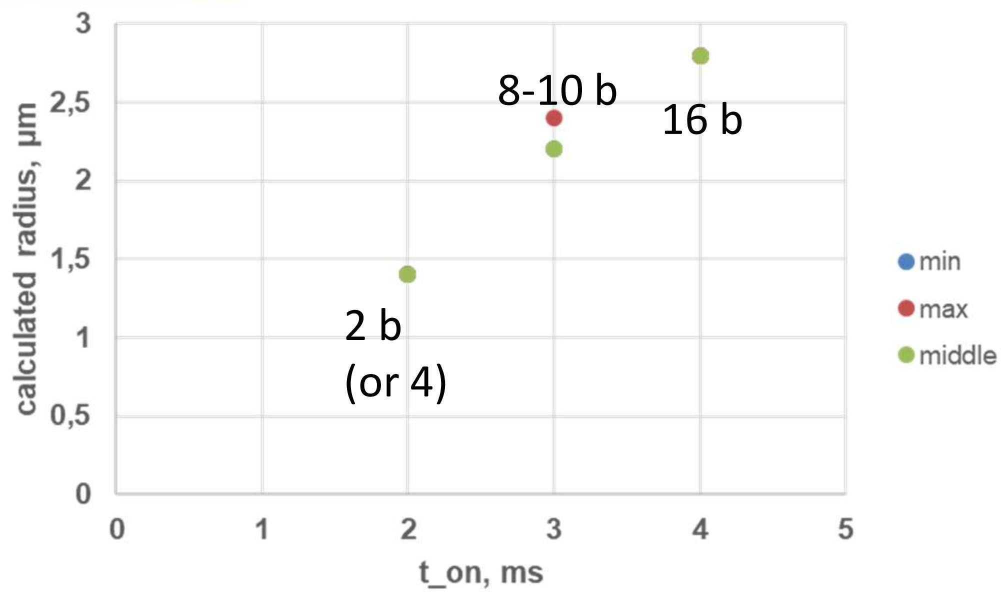
Change in slope already observed for t_{on} = 1 ms, indicating interactions between bubbles.

Smallest measured size: 3.5 µm

An initial radius of **2.8 µm** (= 3.5 / $\sqrt[3]{2}$) allows to interpret experimental values for the different t_{on}.

N_2





t_{on} = 1 ms: SL too dim

t_{on} = 2 ms: I_{SL} increases continuously during the US irradiation then decreases

t_{on} = 3 ms: change in slope after ≈ 1.8 ms → coalescence

very narrow bubble size distributions

Yet, intense coalescence

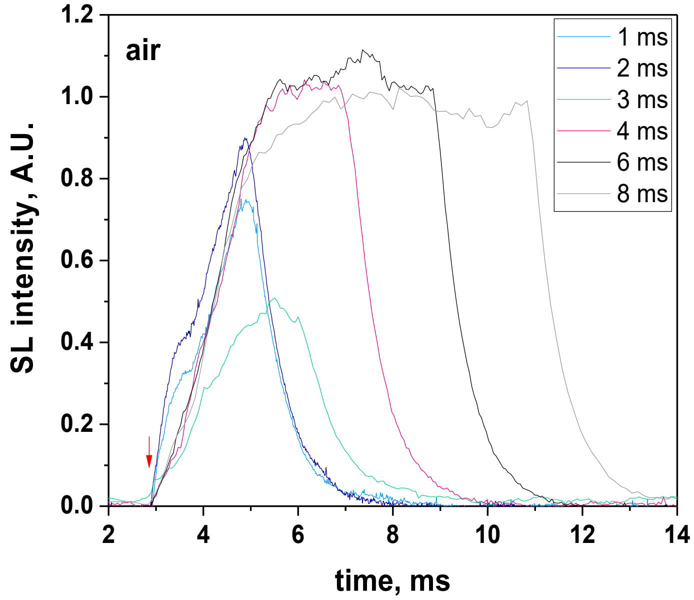
2.2 µm: coalescence of 4 1.4-µm bubbles

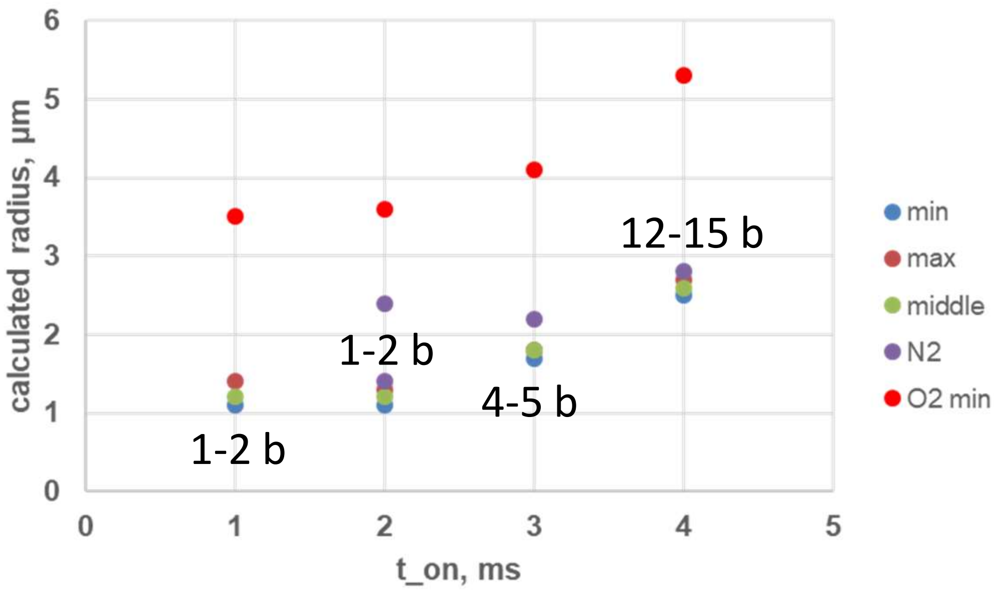
2.8 µm: coalescence of 8 1.4-µm bubbles (or of 2 previously formed 2.2-µm bubbles)

The smallest measured size, 1.4 µm, can be derived from the coalescence of two **1.1-µm** bubbles, or four **0.88-µm** bubbles

→ *close to the Blake threshold*

air





Coalescence already observed for t_{on} = 1 ms
The SL intensity increases during 2 ms: it first reaches a plateau after 1 ms then increases again

Values << O_2 values, close to N_2 ones but smaller: smaller extent of coalescence.

The minimum measured value of **1.1 µm** allows to explain the different radius values obtained (obviously, 0.88 µm too) → *close to the Blake threshold*

air

In agreement with literature values:

Labouret and Frohly, 350 kHz: 2-3.5 µm (bubbles < 2 µm not accessible to the measurement)

Iida et al. (laser diffraction and pulsed sonication, 443 kHz, 5 mM SDS): mean radius of 3.6 µm (but sizes < 2 µm not accessible to the measurement)

Bubble sizes previously determined with the present technique were most of the time also impacted by coalescence, due to the too long t_{on}. Nevertheless:

Lee et al.: 515 kHz, t_{on} = 4 ms

- water: 2.8-3.7 µm
- 1.5 mM SDS: 0.9-1.7 µm

Brotchie et al.: bubble size depends on the pulse width;

- 2.5 µm for t_{on} = 1 ms
- 3.8 µm for 4 ms
- extrapolation to 0 ms: 1.2-1.8 µm

Yasui et al. calculated R_0 in the range 0.3-8.0 µm for SL bubbles in air-saturated water at 300 kHz

Y. Iida, M. Ashokkumar, T. Tuziuti, T. Kozuka, K. Yasui, A. Towata, J. Lee, Ultrason. Sonochem., 17 (2010) 473-479
J. Lee, M. Ashokkumar, S. Kentish, F. Grieser, J. Am. Chem. Soc., 127 (2005) 16810-16811
A. Brotchie, T. Statham, M.F. Zhou, L. Dharmarathne, F. Grieser, M. Ashokkumar, Langmuir, 26 (2010) 12690-12695
K. Yasui, T. Tuziuti, J. Lee, T. Kozuka, A. Towata, Y. Iida,, J. Chem. Phys., 128 (2008) 184705.

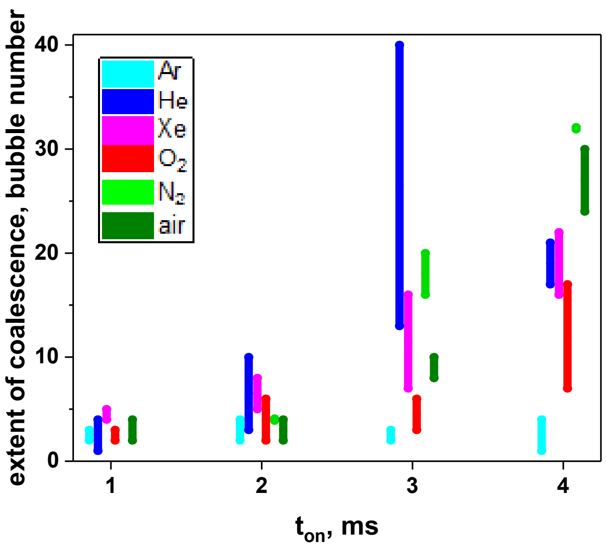
conclusion

For every studied saturating gas, **increasing the pulse on-time leads to the measurement of coalesced bubbles**

Reducing the on-time to a minimum and/or adding SDS to water allows to reduce coalescence so that natural active cavitation bubble sizes can be measured

Obtained radii for pre-saturated water at 362 kHz are:

- **3.0 µm for Ar**
- **1.2 µm for He**
- **3.1 µm for Xe**
- **2.8 µm for O_2**
- **around 1 µm for N_2 and air**



The extent of coalescence strongly depends on the gas nature. No single physical property of the gas allows to explaining it, but it seems to increase with the gas solubility, and also to be favored by a high gas diffusion coefficient

Thank you

for your kind attention!