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# Evidence for liquid phase reactions during single bubble acoustic cavitation

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## Abstract

We extended the recent experiment by Lepoint et al. [Sonochemistry and Sonoluminescence, NATO ASI Series, Series C 524, Kluwer Academic Publishers, Dordrecht/Boston/London, 1999, p. 285], involving a so-called single bubble sonochemistry process, to a three-phase system. We have found experimental evidence that a single cavitating bubble can activate the oxidation of  $I^-$  ions after the injection of a  $CCl_4$  liquid drop in the bubble trapping apparatus. The solvent drop ( $CCl_4$  is almost water insoluble) is pushed towards the bubble position and forms a thin film on the bubble surface. When the acoustic pressure drive is increased above 100 kPa, the three-phase system gives rise to a dark filament, indicating the complexation reaction between starch (added to the water phase) and  $I_2$ .  $I_2$  species is the product of surface reactions involving bubble-induced decomposition of  $CCl_4$ . Further increase of the acoustic drive causes the thin  $CCl_4$  film to separate from the bubble and stops  $I_2$  production. The study of the chemical activity of this three-phase system could give new advances on dynamics of the bubble collapse.

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## 1. Introduction

As the discovery of single bubble sonoluminescence (SBSL) boosted scientific activity about light production by cavitation, so single bubble sonochemistry offers a unique opportunity for a better comprehension of the role of bubble activity in enhancing or quenching particular chemical reactions. The study of chemical activity near—and inside—the bubble can shed some light on controversial aspects of bubble dynamics: for example it is possible to test, to some extent, the reliability of spherical collapse models and some conclusions about the interaction between gas and liquid phases can be derived.

## 2. Experimental apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. It consists of a conventional SBSL setup: a 100 ml spherical quartz flask was driven at 29.3 kHz by a PZT transducer glued to the bottom of the

flask. Bubble activity was monitored by a small piezo-ceramic disk mounted 90° apart with respect to the main PZT driver. This “pick-up” microphone was calibrated against a B&K 8103 hydrophone. The flask was filled with a degassed sample of Weissler's reagent, prepared by adding 10 ml of 10 vol% starch aqueous solution to 200 ml of 1 M KI solution. The third component of the Weissler's reagent,  $CCl_4$ , was added later, with the procedure which will be described in the following section. Bubbles were injected into the flask using a short Ni–Cr wire as a heater. When the stationary acoustic field is present, micron-sized bubbles are pushed by Bjerknes radiation forces towards the main pressure antinode (positioned near the geometrical centre of the spherical flask) and forced into non-linear radial oscillation. This experimental apparatus allowed bubbles trapping in the acoustic pressure range from 60 to 150 kPa. Typically sonoluminescence was produced when the acoustic pressure exceeded 120 kPa. Light emission was detected by a Hamamatsu R7400 photomultiplier tube. The radial bubble dynamics was monitored by a Mie-scattering optical device which exploited a low power, c.w. He–Ne laser (the same photomultiplier tube was used to detect SL pulses and scattered laser light)

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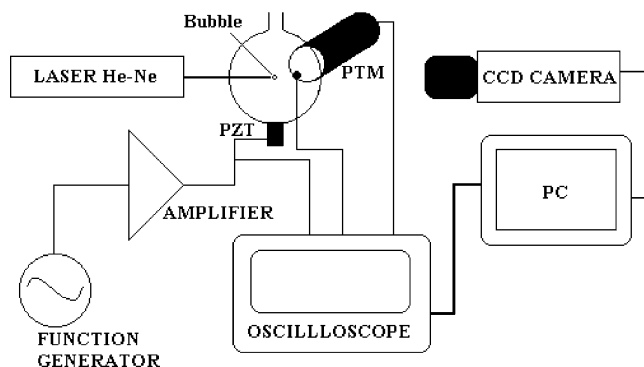


Fig. 1. Apparatus for single sonoluminescing bubble levitation and Mie-scattering measurement devices.

[2]. During Mie-scattering measurements, a bigger spherical flask (500 ml, 16.5 kHz resonant frequency) was used to improve levitation stability and signal-to-noise ratio. A CCD camera, coupled to a stereoscopic microscope, was used to record the translational motion of acoustically levitated bodies (bubbles and drops) and to monitor chemical activity inside the cell.

### 3. Experiments and observations

As pointed out by Lepoint's group [1,3], a single cavitating bubble can induce a chemical reaction. If the cell is loaded with the Weissler's standard solution (i.e., the iodide–starch solution saturated by  $\text{CCl}_4$ ) and a single air bubble is seeded, a weak blue thread can be observed originating at the bubble position. This blue trace indicates the production of the  $\text{I}_2$ –starch complex. The formation of  $\text{I}_2$  is due to the oxidation of  $\text{I}^-$  by  $\text{Cl}(\cdot)$  atoms released during single bubble activity. The sequence of reactions is the following:



where the symbol  $\xrightarrow{\text{acoustic}}$  indicates chemical reactions activated by acoustic cavitation.

An example of the blue thread is shown in Fig. 2; its direction and orientation was observed to change during the experiment, perhaps due to convective currents caused by a non-uniform temperature distribution within the liquid medium.  $\text{I}_2$  production was observed also during SBSL regime, showing that light emission can take place while the trapped bubble is releasing  $\text{Cl}(\cdot)$  atoms in the host solution.

We followed a different experimental procedure. The  $\text{CCl}_4$  was not present as a solute in the reagent filling the cell as in [1,3], but was added as a separate liquid phase ( $\text{CCl}_4$  is almost water insoluble). A thin layer of this substance was gently poured over the free surface of the water solution by a syringe: despite the higher density of

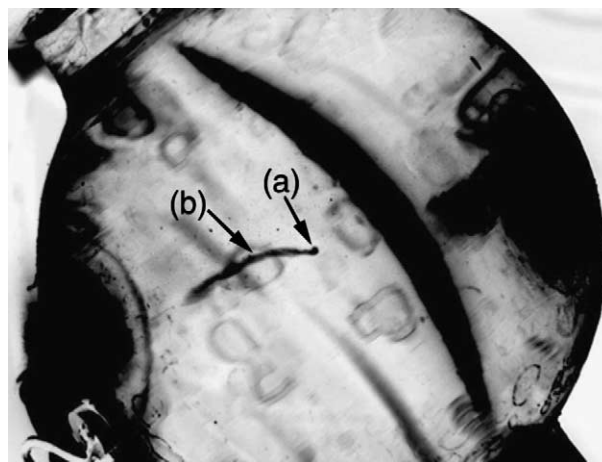


Fig. 2. A single cavitating bubble (a) (the picture represents the bubble during the jittering phase) producing the starch complexed  $\text{I}_2$  filament (b).

$\text{CCl}_4$  with respect to water, the thin solvent film could float on the water surface without sinking. Shaking gently the Ni–Cr heater near the water/ $\text{CCl}_4$  interface, a drop of  $\text{CCl}_4$  formed and was driven by the acoustic pressure towards the centre of the resonant cell. In the presence of the  $\text{CCl}_4$  drop, a gas bubble was seeded. In these conditions (see Fig. 3), the bubble seated in a levitating (or also sonoluminescing) state near the drop, but did not produce any dark filament. Increasing the acoustic pressure, the bubble slowly moved towards the  $\text{CCl}_4$  drop and merged, thus forming a three-phase system, with a thin liquid shell of  $\text{CCl}_4$  separating the gaseous core from the outer water solution. About 3 s after the bubble had entered the drop, the  $\text{I}_2$  thread appeared (Fig. 4). If the acoustic pressure was further increased to reach a sonoluminescing state for the  $\text{CCl}_4$ -coated bubble, the thin film separated and sank to the

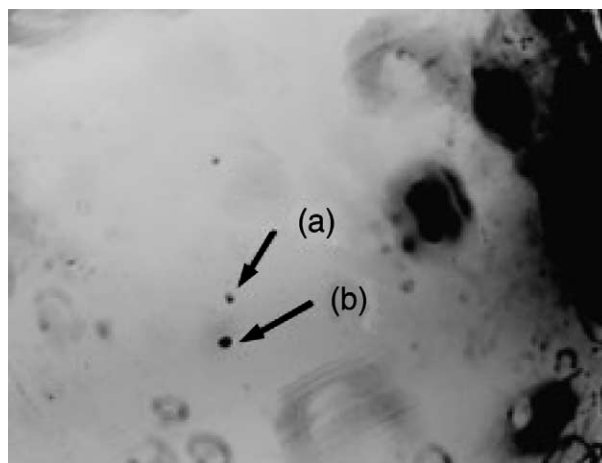


Fig. 3. A translating bubble (a) approaching the  $\text{CCl}_4$  drop (b) (the size of the drop was about  $80\ \mu\text{m}$ ) trapped in the resonant cell. The bubble does not produce any thread, nor does the  $\text{CCl}_4$  drop.

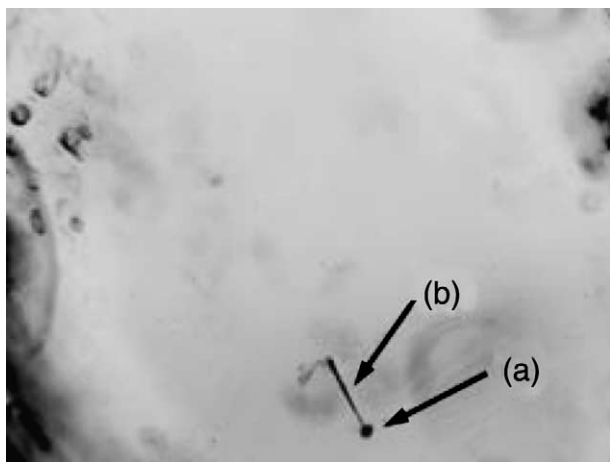


Fig. 4. The three-phase system formed when the gas bubble enters the  $\text{CCl}_4$  drop (a). After a few seconds, a dark filament is released (b).

bottom of the flask, causing the chemical reaction to stop.

#### 4. Properties of the three-phase system

The behaviour of the three-phase system described in the previous section was affected by a certain degree of instability. Only a limited range of acoustic pressure values allowed the coexistence of bubbles and  $\text{CCl}_4$  droplets in the cell. After the gas bubble had entered the drop, it was not possible to observe light emission, even if the acoustic pressure level was compatible with sonoluminescence in standard SBSL conditions: the dynamics of the bubble was strongly influenced by the presence of the coating layer of  $\text{CCl}_4$ . To analyse the radial oscillations of “pure”  $\text{CCl}_4$  drops or gas-filled drops, we accomplished a Mie-scattering measurement. As a test experiment, we measured the light scattered by the sonoluminescing bubble in a 1.0 M KI, 10 vol% starch solution. The results, shown in Fig. 5, reproduce the characteristic signal of SBSL. After this preliminary test, the light scattered by an acoustically trapped  $\text{CCl}_4$  drop was measured in two different conditions:

- in the absence of the blue filament;
- during the production of the blue filament, after the gas bubble had merged into the  $\text{CCl}_4$  drop.

As shown in Fig. 6, the three-phase system oscillates radially and so does the “pure”  $\text{CCl}_4$  drop, measured in the absence of chemical reaction. Since the liquid phase is almost incompressible, we expected to observe only shape oscillations. These results seem to indicate that a little amount of air is present inside the drop—in the form of a gas core—since it was released in the cell. This hypothesis would explain the low acoustic pressure level

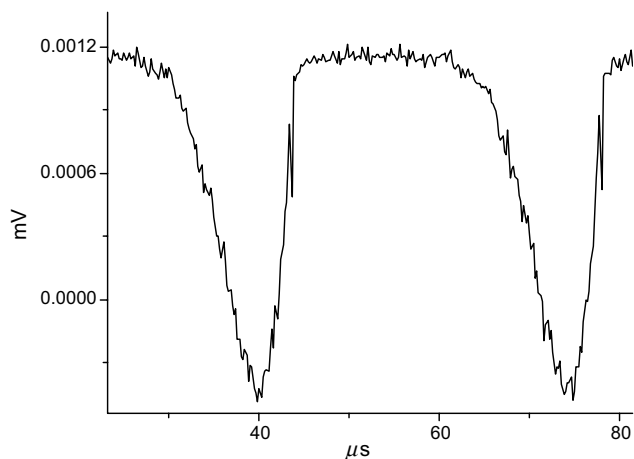


Fig. 5. The typical oscilloscope trace produced by a sonoluminescing bubble when monitored by the Mie-scattering apparatus.

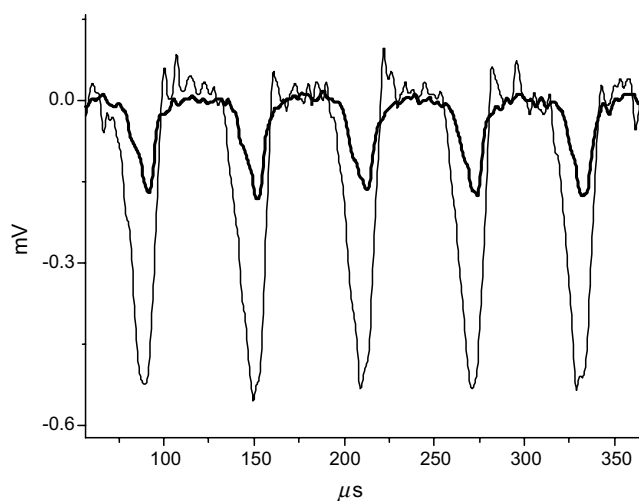


Fig. 6. Mie-scattering signal from the three-phase system just after the formation process (thick line) and after the spontaneous fusion with an air bubble (thin line).

necessary to trap the droplet in the ultrasonic resonator. In accordance with the theory of acoustic radiation pressure on spherical, nearly incompressible bodies immersed in liquid media [4,5], a pure  $\text{CCl}_4$  drop would be trapped near the antinodes of an acoustic stationary field only if the sound amplitude reached the threshold of about 1.5 MPa [5], since carbon tetrachloride is denser than water. The maximum acoustic pressure level measured during the experiments described in this work was about 0.13 MPa, an order of magnitude lower than that trapping threshold. On the other hand, our observations confirm that drops and bubbles behave in the same way as far as the acoustic radiation pressure is concerned: if a non-radial stationary wave pattern is excited in the resonator (so that multiple node–antinode regions are present), bubbles and drops converge towards the same antinode points. A further evidence for

the gas core hypothesis is that if the drop was levitated for more than 5–6 min in stationary acoustic pressure conditions, it spontaneously sank to the bottom of the cell. This phenomenon is probably due to the slow dissolution of the gas core inside the drop: the  $\text{CCl}_4$  coating film interferes with the mass transfer process from the host liquid (water) to the gas core and inhibits the rectified diffusion mechanism. If gas is added to the drop core by bubble injection, it is possible to prevent the (long-term) drop precipitation: the amplitude of the radial oscillation increases and the system finds a stable mass transfer equilibrium point. In our opinion, the relevant parameter is the carbon tetrachloride to gas volume ratio in the droplet. When the drop is created (shaking the heater near the free surface of the water solution), the gas content is hardly sufficient to allow levitation, the “drop” oscillates radially with a very low amplitude and no chemical reaction is possible (see Fig. 6, thicker trace). As soon as a gas bubble merges into the drop, lowering the  $\text{CCl}_4$ /air volume ratio, the oscillation becomes wider, the collapse phase more violent and the production of  $\text{Cl}(\bullet)$  atoms starts, causing the oxidation of  $\text{I}^-$  and the formation of the blue filament.

If the framework outlined above is correct, the activation of  $\text{CCl}_4\text{--I}^-$  reaction needs the presence of a cavitating gas phase; our observations do not agree with the direct oxidation of  $\text{I}^-$  by pure  $\text{CCl}_4$  drops as proposed in [6]: levitating carbon tetrachloride “drops” are actually solvent-coated gas bubbles and the oxidation reaction does not start if the cavitation effects (directly correlated to the radial oscillation amplitude of the “droplets”) are not sufficient to produce radicals.

It is possible to explain the observations exposed in the previous section following two alternative models, sketched in Fig. 7a and b:

- $\text{CCl}_4$  enters the gas bubble as a vapour phase (the vapour tension of  $\text{CCl}_4$  is higher than that of water), then is heated and decomposed during the adiabatic phase of the bubble collapse (Fig. 7a);
- $\text{CCl}_4$  is squeezed in the bubble as a microdrop spray after liquid jets have formed inside the gas phase, at the end of the fast moving interface dynamics (Fig. 7b).

Both the mechanisms lead to the production of chlorine radicals ( $\text{Cl}\cdot$ ), which diffuse and react with  $\text{I}^-$  ions. While the first hypothesis is compatible with a perfectly spherical collapse model, the second involves a non-spherical dynamics. As pointed out by Prosperetti [7], in standard gravity conditions, buoyancy forces and time-dependent Bjerknes forces cause a levitating bubble to move around an equilibrium point. Due to the momentum conservation principle, a translating and collapsing bubble cannot retain a spherical symmetry: the final stages of the collapse are characterised by the for-

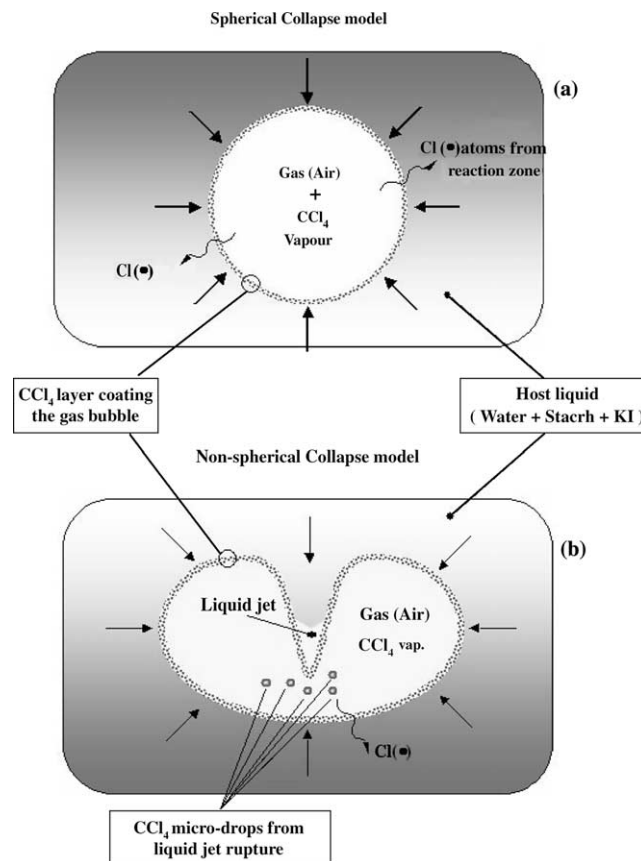


Fig. 7. Two possible mechanisms for chlorine radicals production during the three-phase system collapse.

mation of high speed liquid jets. Some recent experiments seem to validate the non-spherical collapse model: working with  $\text{CS}_2$ , Lepoint's group [3] traced the hydrodynamic flow around a single oscillating bubble and Longuet-Higgins [8] found a better fit of these experimental data if a non-spherical collapse model was assumed. Lepoint [1] also noted a greater chemical activity from a single cavitating bubble when it was in the so-called “jittering” phase or in the presence of “shuttlecock” structures: these states are associated with a highly non-spherical bubble dynamics.

The symmetrical collapse model depicted in Fig. 7a does not seem to be validated by our observations on the three-phase system: as shown in Fig. 2, the drop can levitate near the bubble but no blue thread is produced. In these conditions, a little amount of  $\text{CCl}_4$  can freely diffuse from the drop to the bubble surface, so that reactants are present but the reaction is not activated. Nor the filament is generated at the drop surface, probably because the low amplitude oscillations of the gas core are not sufficient to generate the cleavage of C–Cl bond. After the bubble injection, the amount of air inside the drop grows and the reaction starts. The production of chlorine radicals exclusively after the formation of the three-phase system let us suppose that  $\text{CCl}_4$  is involved

directly in a liquid phase form. This would be possible only if the bubble (or drop) dynamics gets the solvent to touch the hot gaseous content. Non-spherical collapse and liquid jets formation are good models for this process.

## 5. Conclusions

We presented some observations about the sonochemical properties of a three-phase system which consisted of a gaseous bubble separated from a host aqueous solution by a thin layer of carbon tetrachloride. Various interaction phenomena are possible between these solvent-coated bubbles and other gas bubbles or solvent drops present in a resonant ultrasonic trap. We found that the cleavage of C–Cl bonds and the production of free radicals are possible only when the mechanical activity of the system, here defined as the radial oscillation amplitude monitored by a Mie-scattering apparatus, reaches a suitable level. The relationship between mechanical activity and external forcing pressure is strongly influenced by the mean volume of the gas phase present in the tetrachloride-coated bubble. If the gas content is too low, the oxidation reaction of iodide ions is not activated. The same absence of reactivity is observed when a cavitating or sonoluminescing gas bubble lies near, but outside, the (inactive) three-phase droplet. These observations confirm that a direct

reaction between pure, micron-sized, tetrachloride drops and aqueous solution is not possible ( $I_2$  production is a cavitation-mediated reaction, in this experimental set-up), but suggest a possible role of liquid jets and sub-micron liquid spray in single bubble sonochemistry. Of course, the complex behaviour of the three-phase system could be completely different from what has been reported in [1,3], even if the final macroscopic effect is the same, i.e. the production of  $I_2$  in the form of a filament originating from an acoustically levitated body. This work shows how the interface between highly compressed gas inside a bubble and a reactive external liquid layer can reveal unexpected properties.

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