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An investigative study into an oscillatory reaction in acoustically levitated droplets†

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For the first time we have studied an oscillatory chemical reaction (the well-known Belousov–Zhabotinsky (BZ) reaction) in acoustically levitated droplets. Acoustically levitated droplets allow wall-less reaction studies, reduce consumption of sample/reagents, offer high throughput measurements, and enable environmentally friendly chemistry by significantly reducing plastic waste. In this work, microdroplets of the BZ reactants were mixed at the central axis of a low-cost acoustic levitator. The chemical reaction observed in acoustically levitated droplets proceeded in the same way as that in both stirred and unstirred vials where the volume of droplets was 750-fold lower than the solutions in vials. The observed oscillation frequency in droplets was lower than that observed in vials, possibly as a result of evaporative cooling of the droplets. This work has shown that oscillatory reactions can be successfully carried out in acoustically levitated droplets, which allows the application of this technique to areas such as analysis, synthesis and actuation of smart materials and studies of the origins of life.

1 Introduction

Chemical reactions can be performed in droplet microfluidic devices[1–3] to reap benefits such as automation and small volumes.[4] However, in current microfluidic devices, (1) droplets are in contact with either solid walls[5–7] or immiscible liquids,[8] and (2) operations on droplets are conducted on two-dimensional surfaces. While the former can result in loss of sample/reagents and cross-contamination, the latter can limit throughput per unit footprint of devices. These issues can be addressed by performing reactions in droplets levitated in air in three-dimensional space. Furthermore, the use of levitated droplets can reduce laboratory plastic waste, which is currently estimated to be about a thousand kilograms per researcher per year.[9,10]
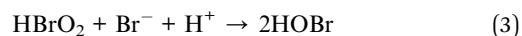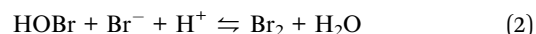
Levitation of droplets requires an upward force sufficient to counteract the downward gravitational force.[11] This upward force can be generated using light,[12] electric[13] or magnetic[14] fields, aerodynamics,[12] and acoustics.[12] The use of acoustics is beneficial because droplets of up to 100 μL of all types of materials can potentially be levitated stably.[15] Acoustic levitators are often formed by placing two surfaces opposite to each other where one surface comprises of ultrasound emitter(s) and the other surface is either a reflector or comprises of ultrasound emitter(s).[11,16] Standing pressure waves are formed between two

oppositely placed surfaces with low pressure regions (*i.e.*, nodes) separated by approximately half a wavelength of the sound waves produced by the emitters.[17,18] Acoustic radiation forces are maximum at pressure nodes. Thus, objects are levitated around pressure nodes. Acoustically levitated droplets have so far successfully been applied for a range of applications including sample preparation,[19] acid–base titrations,[20] synthesis,[15,21] crystallisation,[22] enzymatic assays,[23] and chemical analysis.[21] However, there are no reports on the use of acoustically levitated droplets for performing oscillatory chemical reactions. Oscillatory chemical reactions have applications ranging from analysis[24] to synthesis[25] and actuating[26] smart materials to studying origin of life.[27]

A well-known oscillatory reaction is the Belousov–Zhabotinsky (BZ) reaction.[28–30] Overall, the BZ reaction involves oxidation of malonic acid by bromate ions, and is summarised in eqn (1).[31,32]
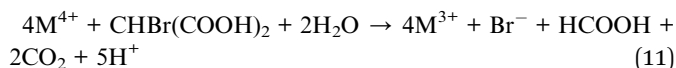
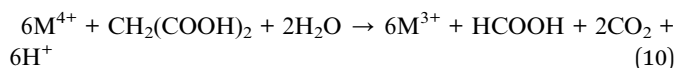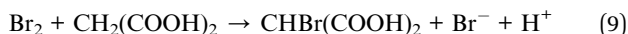$$5CH_2(COOH)_2 + 3BrO_3^- + 3H^+ \rightarrow 3BrCH(COOH)_2 + 2HCOOH + 4CO_2 + 5H_2O \quad (1)$$
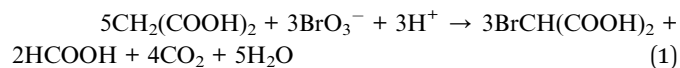
The oscillating reaction consists of ten fundamental interacting chemical reactions,[31] which are provided in eqn (2)–(11). A double arrow indicates a reversible reaction; a single arrow indicates an essentially irreversible reaction.

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \quad (2)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \quad (3)$$

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \quad (4)$$

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$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \qquad (5)$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^\cdot + H_2O \qquad (6)$$

$$BrO_2^\cdot + M^{3+} + H^+ \rightleftharpoons HBrO_2 + M^{4+} \qquad (7)$$

$$BrO_2^\cdot + M^{4+} + H_2O \rightarrow BrO_3^- + M^{3+} \qquad (8)$$

$$Br_2 + CH_2(COOH)_2 \rightarrow CHBr(COOH)_2 + Br^- + H^+ \qquad (9)$$

$$6M^{4+} + CH_2(COOH)_2 + 2H_2O \rightarrow 6M^{3+} + HCOOH + 2CO_2 + 6H^+ \qquad (10)$$

$$4M^{4+} + CHBr(COOH)_2 + 2H_2O \rightarrow 4M^{3+} + Br^- + HCOOH + 2CO_2 + 5H^+ \qquad (11)$$
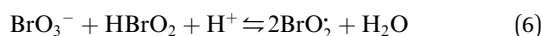
Where M is a suitable metal ion. The oscillating reaction consists of three main processes. Process 1 is the reduction of bromate to bromine by the three steps in eqn (2)–(4) and the concomitant production of bromomalonic acid *via* eqn (9). Process 2 is the reduction of bromate by bromous acid *via* eqn (5) and (6). Process 3 is the reduction of the metal ion catalyst *via* the reactions in eqn (8), (10) and (11). Process 1 decreases the concentration of bromide, and once this concentration falls below some threshold, process 2 begins to dominate and bromous acid starts to reduce bromate. As this occurs, the concentration of M^{4+} increases rapidly *via* eqn (6) and (7), thus increasing the rate of process 3 which in turn increases the concentration of bromide. As the bromide concentration varies, either process 1 or 2 dominates the reaction, resulting in oscillations in the relative concentrations of M^{4+} and M^{3+} thus causing cyclic changes in the colour of the solution. Commonly cerium(IV) ammonium nitrate is used as the metal catalyst, resulting in the colour of the BZ reaction solution oscillating between yellow and colourless. To make the colour oscillations more prominent, ferroin (*i.e.*, tris(1,10-phenanthroline) ferrous sulphate) can be added. In this case, BZ reaction solutions undergo four colour oscillations as species are oxidised and reduced.

The BZ reaction has been studied in droplets, but in all the previously reported studies the droplets were in contact with solid walls and/or with an immiscible carrier fluid. Delgado *et al.*[33] produced uniform 1 nL droplets in a microfluidic device and reported coupling of the reactions in adjacent droplets mediated by exchange of bromine *via* the fluorinated carrier fluid. They also noted that the BZ reaction cannot be carried out in unsaturated carrier fluids as bromine reacts with carbon–carbon double bonds. Similarly, Szymanski *et al.*[34] showed that signals could be propagated by diffusion of bromine between droplets of the BZ reaction mixture suspended in decane as a carrier fluid. Kitahata *et al.*[35] showed that the BZ reaction in a droplet suspended in oleic acid could induce motion of the droplet. In this study, bromine would have been lost from the reaction as oleic acid contains a carbon–carbon double bond. Unlike the present work, in previous work the droplets were unstirred and could lose reactants, particularly bromine, into the carrier fluid.

This is an unprecedented report on the study of an oscillatory BZ chemical reaction in acoustically levitated droplets. We showed that the oscillation period of the BZ reaction in 4 µL levitated droplets is comparable to 3 mL solutions in vials. Equally, we showed that multiple acoustically levitated droplets of BZ reaction solutions can be studied with high reproducibility and repeatability. Thus, the reported approach of performing reactions in acoustically levitated droplets when used in combination with automated fluid sampling methods will be well suited for high-throughput experimentation.

2 Experimental

2.1 Chemicals and materials

Sulphuric acid (H_2SO_4), malonic acid ($CH_2(COOH)_2$), potassium bromate ($KBrO_3$), potassium bromide (KBr), cerium(IV) ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$), iron(II) sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$), and 1,10-phenanthroline were purchased from Sigma-Aldrich. The components of the TinyLev device were bought from eBay and assembled in-house.

2.2 Instrumentation

To study the BZ reaction in acoustically levitated droplets, the TinyLev device (see Fig. 1) reported by Marzo *et al.*[36–40] was used. The main structure of the levitator was 3D printed with polylactic acid (PLA) filament and comprised of two curved surfaces placed ~15 cm apart. Each curved surface had a total of 36 ultrasonic emitters (MSO-P1040H07T, Manorshi) arranged in rings of 6, 12, and 18 with hexagonal packing. Each emitter was 10 mm in diameter and produced sound waves of 40 kHz, which corresponds to a wavelength of 8.65 mm in air. Thus, the minimum separation distance between levitated objects was ~4.32 mm. The ultrasound emitters were driven by a square wave with peak-to-peak voltage of up to 20 V, which was generated using a combination of an Arduino Nano and a L298N Dual Motor Drive board. The acoustic levitator was placed inside a black box. Images were captured using a CMOS
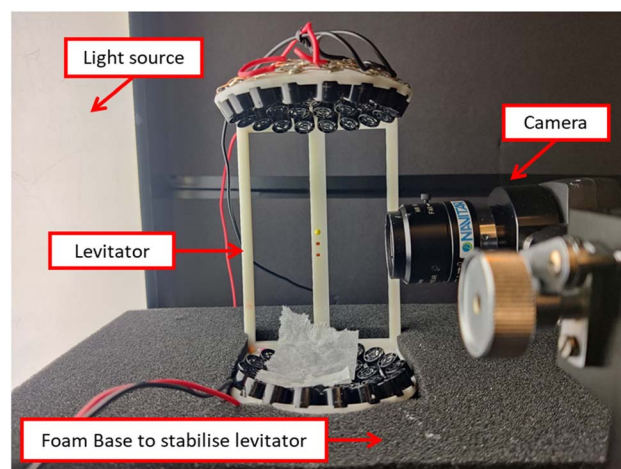

Fig. 1 Schematic of the TinyLev integrated with absorption measurements where each ultrasound emitter is about 10 mm.

camera (UI3580LE-C-HQ with an imaging area of 4.2 × 5.6 mm^2 and pixel size of 2.2 × 2.2 μm^2, iDS Imaging) and lens (MVL25M23, Thorlabs). A daylight wafer light box (model number: D/E/U/A 35040, 4 W LEDs) was used as a light source. The light source and camera were placed opposite to each other to measure absorbance of droplets.

2.3 Procedure

Stock solutions of 0.5 M KBrO$_3$, 1 M KBr, 1 M CH$_2$(COOH)$_2$ and 0.5 M Ce(NH$_4$)$_2$(NO$_3$)$_6$ were prepared in 0.9 M sulphuric acid. A stock solution of 0.5% (w/v) ferroin was made by adding 0.024 g iron(II) sulphate heptahydrate and 0.046 g 1,10-phenanthroline in 10 mL 0.9 M sulphuric acid.

To study the chemical oscillator in vials, stock solutions of KBrO$_3$, KBr and CH$_2$(COOH)$_2$ were added in selected volumes in 0.9 M sulphuric acid to make 3 mL solution containing 77 mM, 20 mM, and 100 mM, respectively. The solution in one of the vials was unstirred while the other was stirred at ~300 rpm using a magnetic bar and plate. To both unstirred and stirred vials, stock solutions of ferroin and Ce(NH$_4$)$_2$(NO$_3$)$_6$ were added to obtain final concentrations of 0.05% (w/v) and 8 mM, respectively. We call the resulting solution as 1× mixture (see Table 1). Movies of the reaction in vials were recorded using an Android phone camera at 30 frames per second.

Expanded polystyrene particles were first levitated to serve as a guide for finding the central axis of the TinyLev. Up to five 4 μL droplets of solution containing KBrO$_3$, KBr and CH$_2$(COOH)$_2$ were pipetted in the central axis of the levitator and were successfully levitated. Subsequently, selected volumes of ferroin and Ce(NH$_4$)$_2$(NO$_3$)$_6$ solutions were pipetted into the levitated

droplets. We studied 1× and 2× (double the concentrations of 1× mixture) mixtures in acoustically levitated droplets. A thin piece of tissue was used to cover the transducers on the bottom surface to prevent any damage by falling droplets. Movies of levitated droplets were made using uEye Cockpit software (iDS Imaging) at 4.4 frames per second.

The ImageJ open-source image processing program was used to extract information frame by frame from movies of the droplets. An ImageJ macro was written to pick the centre of either the solutions in the vials or the levitated droplets. The movies were split into a sequence of images, after which each image was separated into blue, green, and red colour channels. An average grayscale value for all three colours were determined over a rectangle of 100 pixels wide and 100 pixels high centred around the picked point. Transmission was calculated by taking the ratio of average grayscale values at a given time and those before adding reagents. Transmissions were then converted to absorbances. Absorbances *versus* time for the green channel showed the greatest change and hence were fast Fourier transformed (FFT) to determine the frequency of oscillations.

3 Results and discussion

3.1 Glass vials

Initially the BZ chemical oscillator was studied in glass vials before carrying out experiments in acoustically levitated droplets. Because it is known[41] that acoustically levitated droplets undergo stirring arising from the levitating acoustic field, the reaction was studied under both unstirred and stirred conditions. As shown in Fig. S1 (in the ESI)† oscillations in colour

Table 1 Composition of 1× mixture

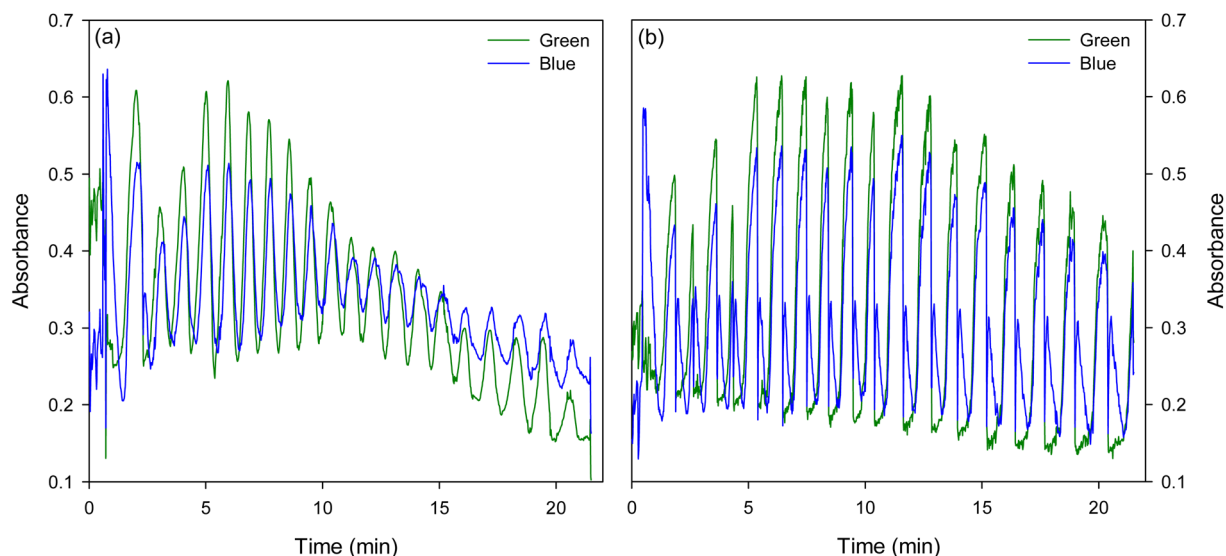| Chemical	H$_2$SO$_4$	KBrO$_3$	KBr	CH$_2$(COOH)$_2$	Ferroin	Ce(NH$_4$)$_2$(NO$_3$)$_6$
Concentration	0.9 M	77 mM	20 mM	100 mM	0.05% (w/v)	8 mM

Fig. 2 Absorbances for the green and blue channels *versus* time for the BZ chemical oscillator (1× mixture) in (a) unstirred and (b) stirred vials.

were observed in both cases, but the unstirred vial shows both temporal and spatial variations in color while the stirred vial is spatially uniform. Similar studies could not be performed for 2× mixture as the absorbance was too high.

Fig. 2 shows the changes in absorbance for the camera green and blue channels as a function of time. Oscillations were clearly visible for both vials, but the amplitude of the oscillations reduced more rapidly for the unstirred vial. This may be a result of the spatial non-uniformity of the unstirred reaction. FFT of all oscillations except the first one in the green channel shown in Fig. 2 was performed, which revealed that the reaction occurred slightly faster in the unstirred vial, with an average
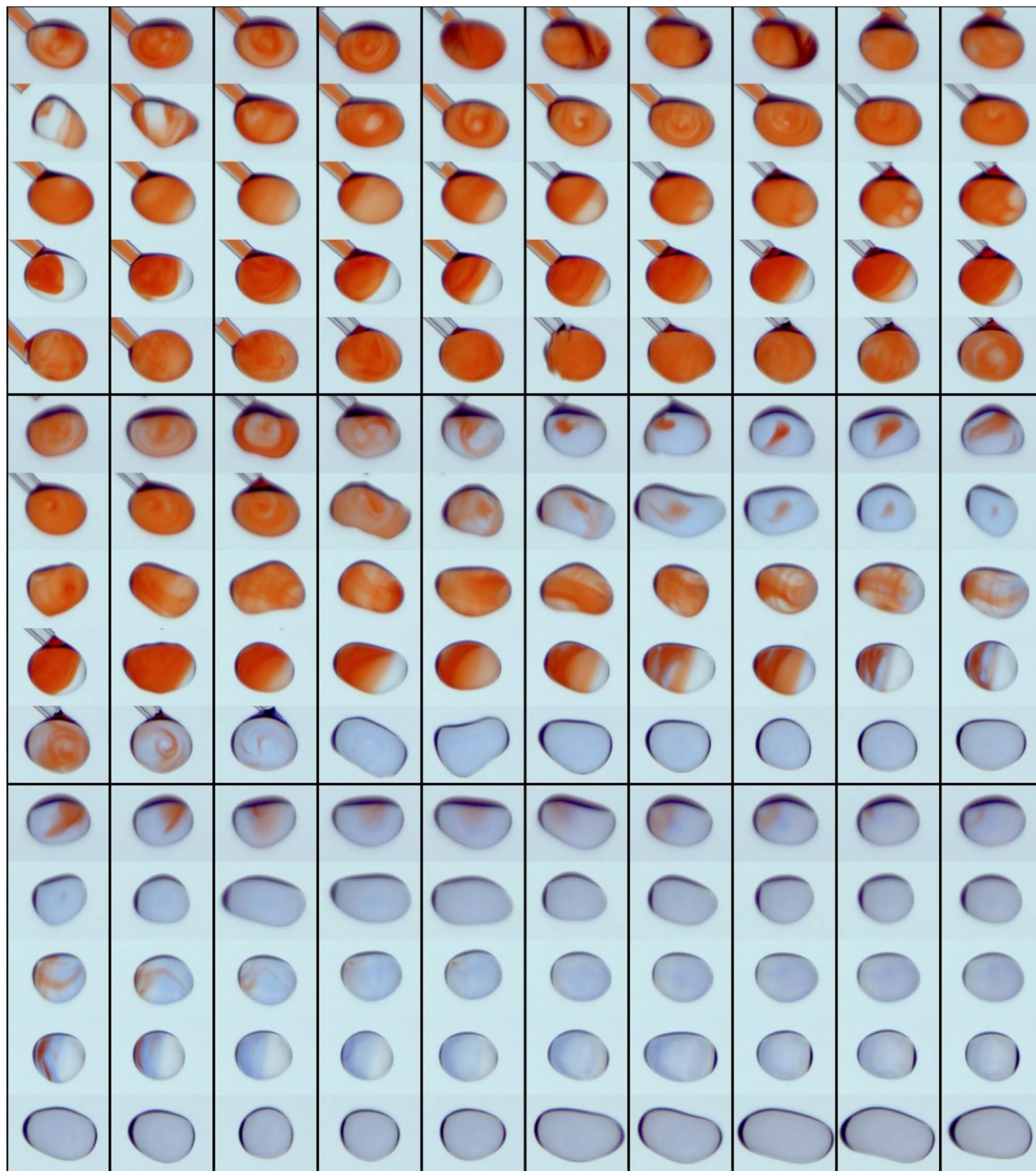

Fig. 3 Montage of images of five droplets levitated simultaneously on addition of the ferroin reagent with a time resolution of 227 ms where the vertical direction is along the central axis of the levitator (images should be read from top left to right and then from top to bottom row, and the size of the box surrounding the five droplets is 3.3 mm by 12.5 mm).

frequency of 1.119 ± 0.008 min^{-1} compared to 0.875 ± 0.017 min^{-1} for the stirred vial. The corresponding average oscillation periods for the unstirred and stirred vials are 0.894 ± 0.006 min and 1.143 ± 0.017 min, respectively. This is in accordance with the observations of Ruoff and Schwitters.[42] Since the reaction proceeded as expected in the stirred vial, it was then carried out in acoustically levitated droplets.

3.2 Acoustically levitated droplets

In this work the initial droplets and subsequent reagent solutions that initiated the BZ oscillator were pipetted manually. Occasionally droplets were lost during this process and the oscillations had to be started sequentially. These limitations can be overcome by integration of acoustic levitators with 3D printed autosamplers similar to one reported previously by the authors.[43]

Fig. 3 shows a montage of images taken at 4.4 frames per second after the addition of the ferroin reagent to five droplets levitated simultaneously, showing the acoustically driven mixing that occurs.

Movie S1† showing the addition of ferroin reagent and acoustically driven mixing is included as a ESI.† In this case, full mixing took at most 6.8 s (30 frames) and showed that the centre of the droplet is only weakly stirred by the acoustic field. This implies that internal flow within acoustically levitated droplets was high around their circumference and minimal at their centre. The internal flow patterns in acoustically levitated droplets observed in this work agree with previous reports.[44] Because the oscillation period is much longer than this mixing time, we can consider that the droplets were fully stirred during the BZ reaction. Significant distortions of the droplet shape lasting about 3.4 s can also be seen after withdrawal of the pipette. Acoustic radiation force on a small spherical particle is calculated from the gradient of Gor'kov potential.[45–47] Changes in the Gor'kov potential are at a maximum along the central axis of the levitator, providing a stronger restoring force in that direction compared to the orthogonal directions. This means that distortions of the droplet are larger in directions orthogonal to the levitator axis, as shown in Fig. 3. This is more pronounced for the droplets furthest from the acoustic focus in the centre of the levitator where the acoustic restoring forces orthogonal to the levitator's vertical axis are weakest.

Fig. 4 is a montage of images of the middle droplet out of the five levitated droplets showing colour oscillations with a time resolution of 1.59 s. Movie S1,† which shows colour oscillations in the five levitated droplets of 2× mixture, is included as a ESI.† Some spatial inhomogeneity in colour is visible in the levitated droplet in the direction perpendicular to the central axis of the levitator, suggesting that mixing in the droplet is not as efficient as in the stirred vial but is better than in the unstirred vial.

Two runs of five droplets of the 1× mixture were carried out. Movie S2,† which shows colour oscillations in the five levitated droplets of 1× mixture, is included as a ESI.† Fig. 5 shows the
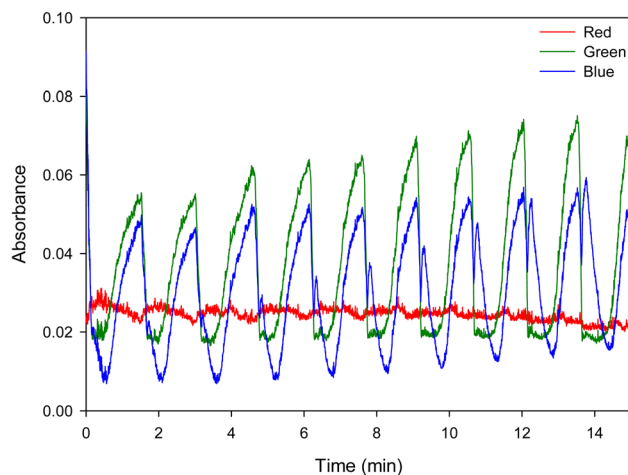

Fig. 5 Plot of the change in absorbance of the red, green and blue channels against time for a typical levitated droplet of 1× mixture.
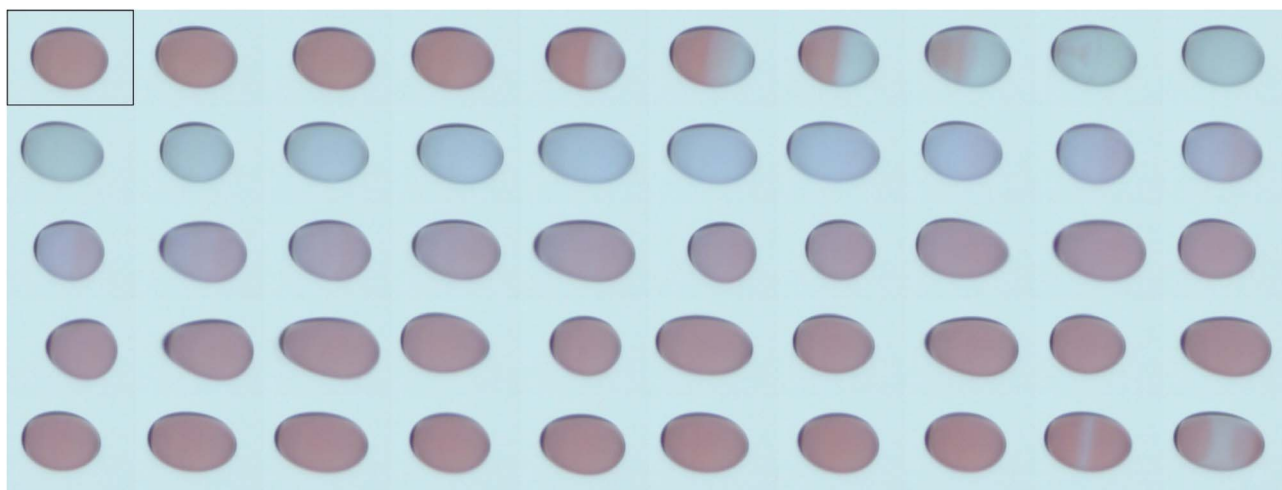

Fig. 4 Montage of images of a single droplet of 2× mixture undergoing oscillations with a time resolution of 1.59 s where the vertical direction is along the central axis of the levitator (images should be read from top left to right and then from top to bottom row, and the size of the box surrounding the droplet is 3.3 mm by 2.5 mm).
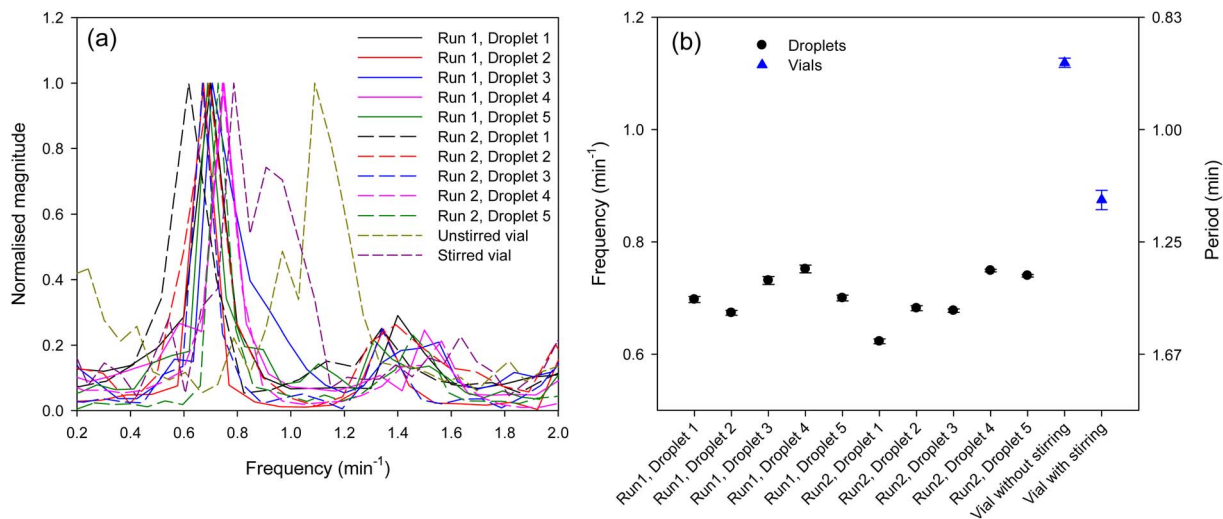
Fig. 6 (a) FFTs of the entire time courses for two runs with five droplets of $1\times$ mixture levitated simultaneously and in the unstirred and stirred vials and (b) scatter plot with error bars (± 1 standard deviation) of the oscillation period derived from the FFTs.
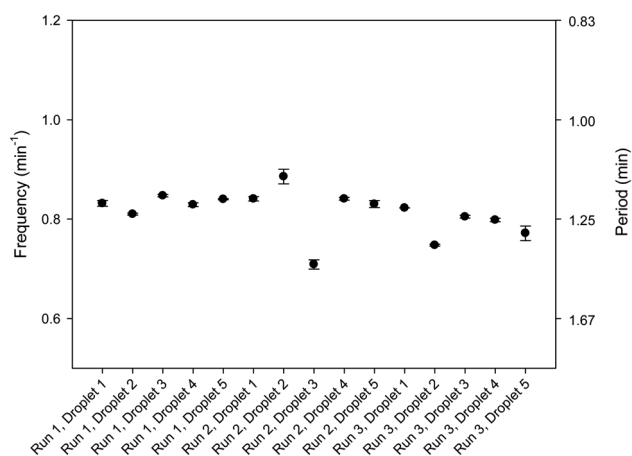

Fig. 7 Scatter plot of the oscillation periods determined from the FFT of the time courses for three runs where, in each run five droplets of the $2\times$ mixture were levitated simultaneously.

change in absorbance for the red, green and blue camera channels as a function of time for a typical levitated droplet of $1\times$ mixture where, the first oscillation is not shown. The red channel shows very little change, as expected based on the observed colour changes. Both the green and blue channels show strong oscillations with a slow rise and rapid fall in absorbance. Similar behaviour was observed for all droplets of both the $1\times$ and $2\times$ mixtures.

FFTs were taken of the entire time courses for the green channel for both runs of five droplets of $1\times$ mixture as shown in Fig. 6(a). In addition, the FFTs of the green channel time courses in the unstirred and stirred vials are also shown in Fig. 6(a). The peaks in the FFTs of the droplet time courses for both runs were clustered together at a frequency of 0.702 ± 0.041 min^{-1}. A t-test carried out between the oscillation frequencies of the two runs (unpaired, two tailed, homoscedastic) suggested that the two runs are not significantly

different ($p = 0.554$). Further t-tests showed that the oscillation frequencies in both the unstirred and stirred vials were significantly different from the oscillation period in the levitated droplets. One possible explanation of the slower oscillation observed in droplets is evaporative cooling[48] reducing the reaction rates as a result of the higher surface area to volume ratio of the droplets. Further work will be required to measure the droplet temperature to determine if this was the cause of the slower oscillations in droplets.

A further three runs where, in each run five droplets of $2\times$ mixture were levitated simultaneously, were carried out and the time courses acquired. These in turn were Fourier transformed to determine the oscillation period. The results are summarized in Fig. 7, giving an overall average frequency of 0.814 ± 0.044 min^{-1}. These results were compared to the results from the $1\times$ mixture using a t-test (unpaired, two tailed, homoscedastic), which showed that the periods for $1\times$ and $2\times$ droplets were significantly different ($p = 1.54 \times 10^{-6}$). This is in accordance with the findings of Suzuki and Yoshida,[49] who showed that increasing the concentrations of malonic acid and bromate increased the oscillation frequency.

4 Conclusions

We have shown that it is possible to study oscillatory reactions such as the Belousov–Zhabotinsky (BZ) oscillator in acoustically levitated droplets. We have obtained results for the oscillation period in acoustically levitated droplets that are consistent with previous work carried out in cuvettes, test tubes, vials and beakers. We have also shown that it is possible to perform multiple simultaneous reactions with good reproducibility and repeatability, thus opening the possibility of using acoustic levitation for high-throughput experimentation. In addition, the solution volume used in the levitator was 4 µL compared to 3 mL in vials, a reduction by a factor of 750, making this method well suited for experimentation with high-cost materials.

This approach to performing oscillatory reactions in levitated droplets using the TinyLev levitator, which is readily available at relatively low cost (~£15) as a kit of parts that can be assembled in a few hours using only a soldering iron and common laboratory tools. A complete experimental setup can be constructed using the TinyLev levitator, a mobile phone (to record images/video) and a low-cost LED light box of the type commonly used by artists (costing between £5–20). This means that the reported platform for acoustically levitated droplets is within reach of resource constrained laboratories.

Future work will focus on increasing the number of levitated droplets and automating the initial loading of the levitator and subsequent addition of droplets to minimise user interventions and errors.

Conflicts of interest

All authors declare no conflict of interest.

Author contributions

Songsaeng acquired data. Gupta and Goddard did conceptualization. Gupta did funding acquisition, project administration, resources, and supervision. All other activities were done by all authors. All authors have given approval to the final version of the manuscript.

Acknowledgements

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