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Emergent properties of the compartmentalised Belousov-Zhabotinsky reaction

Abstract

The Belousov-Zhabotinsky reaction is one of the best known oscillatory reaction and constitutes a model of choice to study the synchronisation of chemical oscillators. In experiments, these micro-oscillators can be micelles, droplets in microfluidic assemblies or catalyst-loaded beads, and the wealth of the patterns found in such systems has drawn much interest in the last decade. Using stochastic simulations, we show that the behaviour of an isolated micro-oscillator also displays emergent properties. More generally, we highlight the existence of emergent phenomena that could be generic to oscillatory systems subjected to fluctuations.

Keywords

nonlinear chemistry, oscillations, micro-oscillator, fluctuations

1. Introduction

When a chemical reaction takes place in a closed system, the concentrations of the reactants and products evolve towards equilibrium concentrations. However, if the system is maintained far from thermodynamic equilibrium by the external supply of reactants or the elimination of products, more complex behaviours can arise. In particular, when the chemical mechanism involves feedbacks like autocatalysis, the differential equations

describing the evolution of the concentrations in the course of time include nonlinear terms [1]. To name a few, oscillations, multistability and chaos are typical phenomena generated by nonlinear chemical reactions maintained out of equilibrium. If the chemical dynamics is further coupled to transport phenomena like diffusion or convection, spatiotemporal patterns can also develop [1].

The Belousov-Zhabotinsky (BZ) reaction constitutes one of the first experimental evidences of the complex dynamics arising from nonlinear chemistry. This reaction was discovered in 1951 by Boris Pavlovich Belousov, who searched for an inorganic analogue of the Krebs cycle. Many other chemical systems including catalytic surface reactions and electrochemical reactions have been shown to generate nonlinear behaviours, but the BZ reaction tends to remain the oscillatory reaction *par excellence*. The BZ reaction has been extensively studied both experimentally and theoretically, in many different setups including stirred batch reactors, gel reactors, membranes, populations of catalyst-loaded beads, reverse (water-in-oil) microemulsions and microfluidic assemblies (BZ droplets) [2–4]. Moreover, a photosensitive version of the reaction has been widely exploited to investigate the effects of illumination on nonlinear dynamics [5]. In this work, we focus more specifically on the emergent properties of BZ microemulsions, which are described in more detail in the next section.

2. The Belousov-Zhabotinsky reaction in microemulsion

In BZ droplets and BZ microemulsions, the reactants are confined in the aqueous phase, which is dispersed into a continuous, hydrophobic phase. The majority of the BZ reactants are polar species that tend to be confined in the aqueous phase. However, some nonpolar intermediates are also involved in the reaction and are likely to move to the surfactant layer or the hydrophobic phase, where they can diffuse and eventually enter another micelle or droplet. A collision-coalescence-redispersion mechanism specific to microemulsions [6] further ensures mass exchange between the micelles. These systems display a variety of spatiotemporal patterns that are not present in the “bulk” case, as shown in Figure 1.

While mass transport is crucial to the emergence of new patterns in the BZ microemulsions,

the role of other compartmentalisation effects like fluctuations remains unclear. In such configurations, the volume in which the BZ reactants are encapsulated is very small and a given micelle only contains a few tens of molecules of the most abundant species. As a result, large fluctuations in the chemical composition of the micelles are to be expected. The extent to which these intrinsic fluctuations perturb the dynamics of this reaction is still poorly understood. In this context, we have analysed the chemical behaviour of an isolated BZ droplet, in the presence and in the absence of fluctuations. More precisely, we compared the behaviour of a single droplet, subjected to fluctuations, to the dynamics of a corresponding bulk system of macroscopic size, where such fluctuations are not observable. We focused on the impact of fluctuations on the photosensitive version of the reaction and investigated the emergence of fluctuation-induced behaviours.

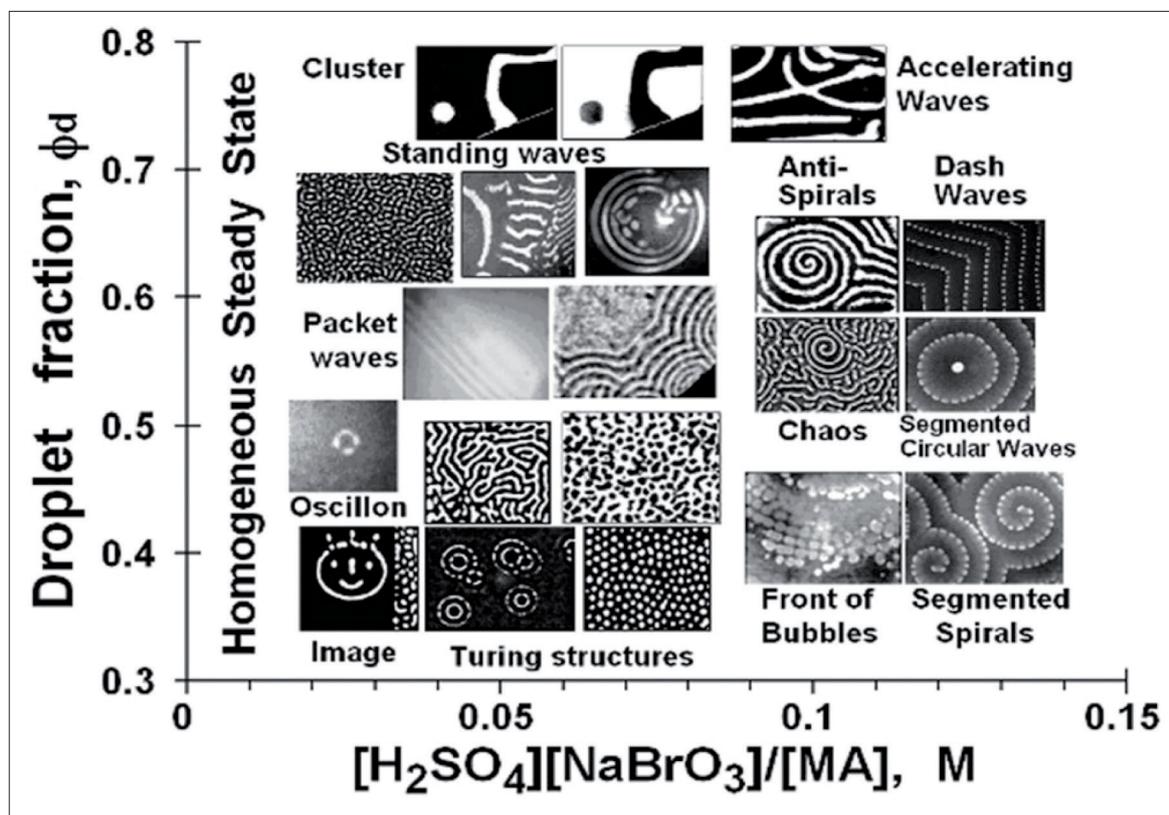


Figure 1: Phase diagram of the behaviours observed in the BZ microemulsions, with respect to the droplet fraction ϕ_d (the volume of the dispersed phase, i.e., water and surfactant, divided by the total volume of the system) and the ratio of the concentrations of key species. Figure reproduced from reference [4].

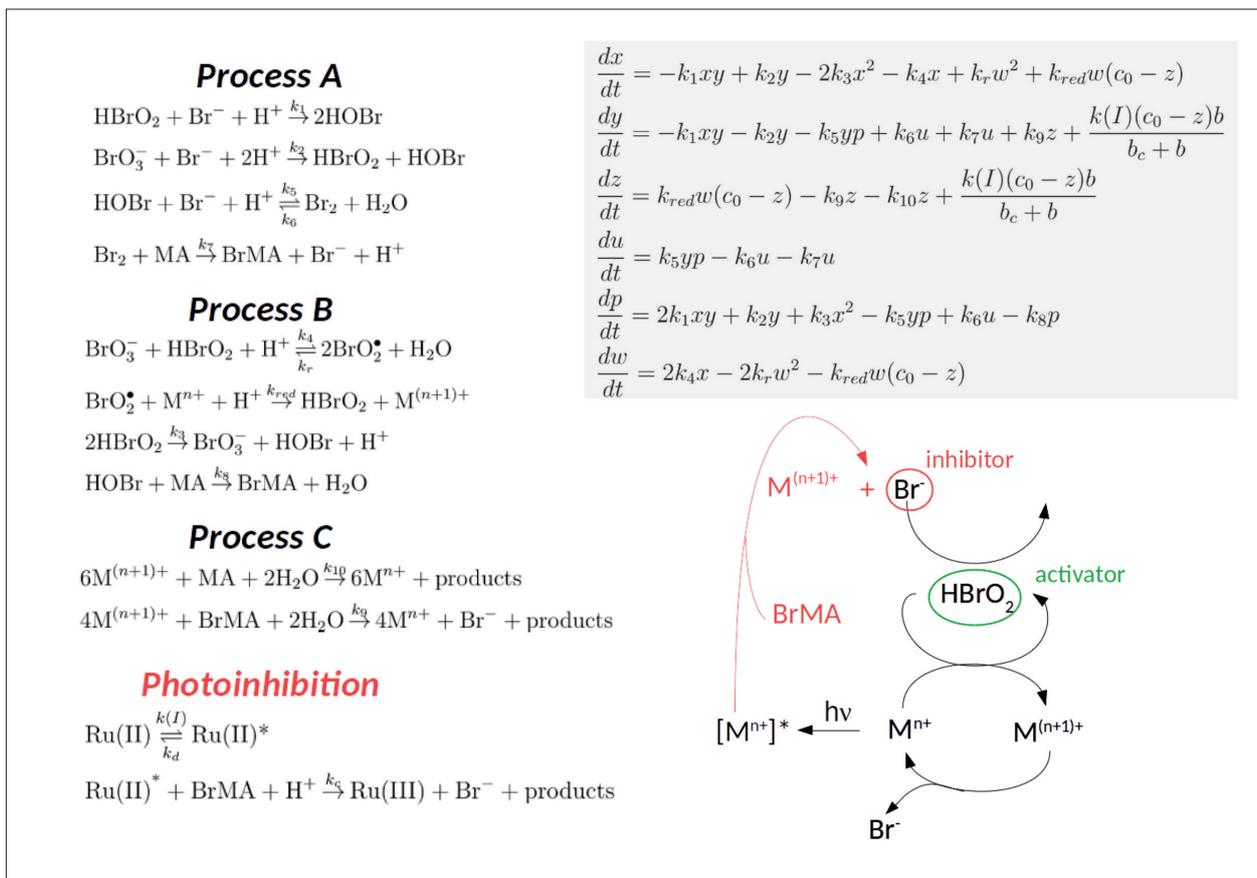


Figure 2: Chemical mechanism of the BZ reaction proposed by Field, Körös and Noyes: (left) chemical equations, (upper right) evolution equations and (lower right) schematic representation of the main feedback loops involved in the mechanism. For clarity, we set the variables $x=[\text{HBrO}_2]$, $y=[\text{Br}^-]$, $z=[\text{M}^{n+}]$, $u=[\text{Br}_2]$, $p=[\text{HOBr}]$, $w=[\text{BrO}_2^*]$ and the constants $c_0=[\text{M}^{n+}]+[\text{M}^{(n+1)+}]$, $b=[\text{BrCH}(\text{COOH})_2]=[\text{BrMA}]$, $b_c=k_d/k_c$, $ma=[\text{CH}_2(\text{COOH})_2]=[\text{MA}]$, $h=[\text{H}^+]$ and $a=[\text{BrO}_3^-]$, which have been incorporated in the kinetic constants.

3. Mechanism and model

The first mechanism for the BZ reaction has been proposed by Field, Körös and Noyes in 1972 [7, 8] and many simplified versions of the model (e.g. the Oregonator [9]) have been developed. This mechanism involves bromine, organic and cerium species and can be decomposed in three processes (Figure 2). Bromide (Br^-) and hypobromous acid (HBrO_2) were respectively identified as the inhibitor and the activator of the reaction. Typically, the reaction mixture initially contains the catalyst, malonic acid, sulfuric acid and a bromate salt, but small quantities of bromide can also be added to reduce the latency period preceding the appearance of the first oscillation [10].

In Process A, the inhibitor is mainly oxidised by different bromine species. The activator is present

in small quantities but is exclusively involved in the oxidation of Br^- . When the inhibitor concentration reaches a critical value, the autocatalysis of the activator becomes the dominant reaction (Process B) and is accompanied by the oxidation of the redox catalyst (M^{n+}). When the reduced form of the catalyst is almost depleted, the autocatalysis stops. Organic species then “reset the clock” in Process C by regenerating the reduced catalyst as well as bromide, which is a key step for the sustainability of the oscillations. Process A can thus start again when the accumulation of bromide is sufficient.

An alternative version of the reaction, which is catalysed by the tris(2,2'-bipyridine)ruthenium(II) complex ($\text{Ru}(\text{bpy})_3^{2+}$), displays photosensitive properties [5, 11]. More specifically, the photoinhibition of the oscillations is frequently exploited in systems of BZ beads or BZ droplets

to control the behaviour of the system [3, 4, 10]. The illumination of the system triggers the formation of an excited form of the catalyst, which reacts with an organic species to generate the inhibitor [11]. The combination of the Field-Körös-Noyes (FKN) and the photoinhibition mechanisms yields a model (see Figure 2) that was shown to efficiently reproduce the dynamics of BZ droplets in microfluidic assemblies for appropriate values of the parameters [10]. We investigated the impact of fluctuations on the chemical dynamics of the photosensitive Belousov-Zhabotinsky reaction on the basis of this model.

4. Fluctuation effects on the dynamics of BZ microreactors

4.1. Behaviour of large and ideal systems

The model presented in Figure 2 describes the evolution of the concentrations in an ideal and macroscopic system, *i.e.*, in the absence of fluctuations. Numerical integrations of these equations have shown that the BZ reaction can be at the source of a multitude of nonlinear behaviours ranging from oscillations to birhythmicity and chaos [12]. In the simplest case, the system undergoes transitions, often

referred to as *bifurcations* in nonlinear systems, from a stationary state to oscillations, then from oscillations to another stationary state, as one of the control parameters is changed (Figure 3a). This is what happens when the reaction takes place in the dark or under illumination with low light intensity. However, if the system is exposed to higher light intensities, oscillations can coexist with the stationary state (Figure 3b).

4.2. Stochastic simulations

To simulate the fluctuating dynamics of the FKN model, we used stochastic simulations that predict the behaviour of the system as a function of the probability associated to each reactive event [13]. This probability directly depends on the size of the system, *i.e.*, on the volume of the droplet. At each iteration, the reaction probabilities are calculated based on the current state of the system (the number of particles of each species) to define the next reaction to occur and the time that will elapse before this reaction. The number of molecules of each species is then adapted, according to the stoichiometry of the selected reaction.

Stochastic simulations showed that fluctuations impact the behaviour of the system in the neighbourhood of the bifurcations in two

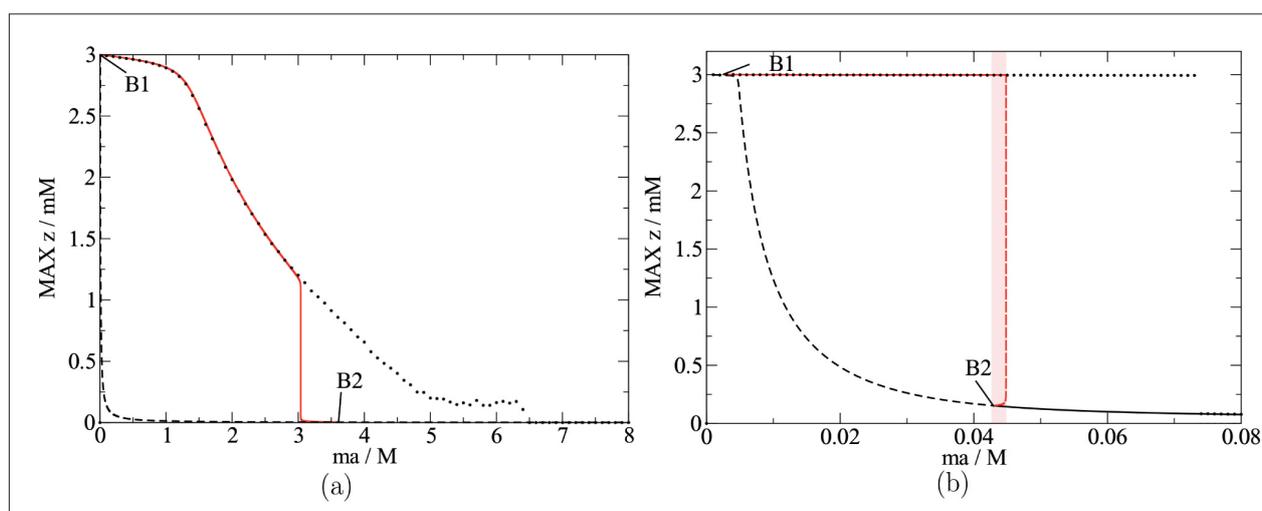
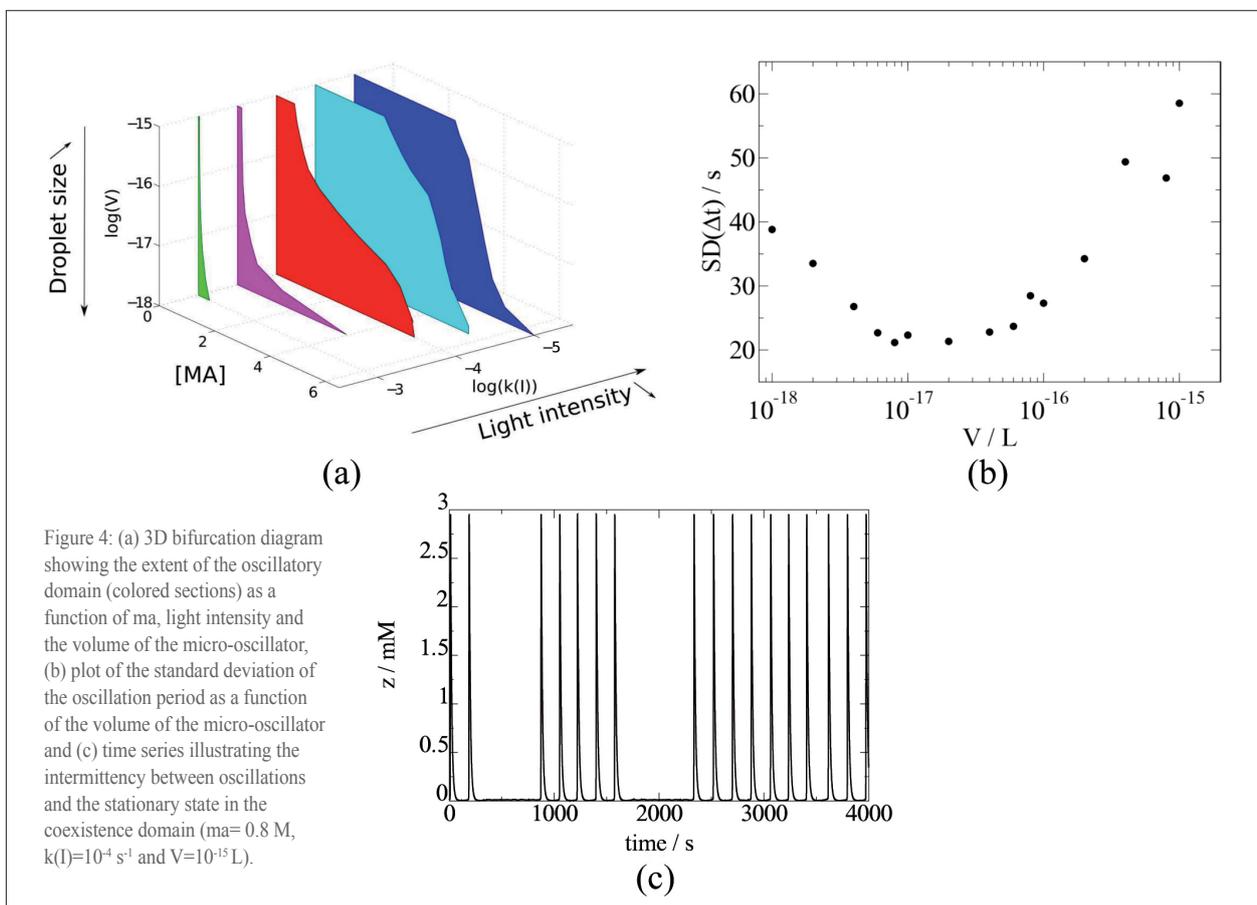


Figure 3: Bifurcation diagrams of z versus ma for (a) low light intensity and (b) high light intensity. The plain lines correspond to stable stationary states and unstable trajectories are represented by dashed lines. The maxima of the oscillations are plotted in red and steady states in black. These results are predicted by the evolution equations shown in Figure 2. The black dots correspond to results of stochastic simulations (maxima of the oscillations or steady states) for $V = 5 \times 10^{-17}$ L. The shaded area corresponds to the domain of coexistence of oscillations and the steady state.

different ways, depending on the light intensity. For low light intensities or in the dark, fluctuations tend to expand the oscillatory domain as indicated by the small dots in Figure 3a. The amplitude of these fluctuation-induced oscillations gradually decreases as the malonic acid concentration is increased, and far from the bifurcation, a noisy stationary state is recovered. The situation is different for high light intensities where oscillations are expected to coexist with a stable steady state for a suitable choice of parameters. In droplets of small volume, large amplitude oscillations exist for a larger range of malonic acid concentration, but in this case, the transition from large amplitude oscillations to the stationary state is much more abrupt (Figure 3b). This difference of behaviour is mainly due to the type of bifurcation leading to oscillations. In both cases, this expansion of the oscillatory domain is particularly relevant for the inhibition of oscillations by light in micro-oscillators. More specifically, our study shows that larger light intensities should be used in small systems

to obtain the same efficiency of photoinhibition as in macroscopic systems (Figure 4a).

We further observed that in the domain of coexistence, there is an optimal system size for which the oscillations are more regular than in small and in large systems. This trend can be quantified with the standard deviation of the oscillation period (Figure 4b). For small BZ micro-oscillators, fluctuations induce frequent transitions between the two attractors, which make the oscillations highly irregular, as expected. However, for large systems, the frequency of oscillations also spreads widely. In such cases, the system is characterised by reaction spikes that are separated by periods of latency, during which the system is in the stable stationary state (Figure 4c). This intermittency is due to fluctuations allowing for transitions between the two coexisting regimes, by driving the system beyond the unstable state that separates them (Figure 2b). When the amplitude of the fluctuations is reduced, these



transitions are less frequent, but the “lifetime” of each behaviour increases. For large systems, the dynamics thus consists in long periods of oscillations followed by long phases of latency, and vice-versa.

5. Discussion

To summarise, we investigated the impact of fluctuations of composition on the oscillatory regime displayed by the BZ reaction in the presence and in the absence of photoinhibition. We distinguished two classes of fluctuation-induced phenomena. The first corresponds to the emergence of oscillations sustained by fluctuations in the neighbourhood of bifurcations. This behaviour crucially impacts photoinhibition, which is thus less efficient than in macroscopic systems. However, this property could also be used to tune the behaviour of the system by acting on the size of the system instead of the concentrations or the light intensity. A second fluctuation-induced behaviour takes place inside the oscillatory domain when large-amplitude oscillations coexist with a stable stationary state. In particular, we showed that the effect of noise on the regularity of the period of oscillations can be minimised for a specific droplet size.

Such fluctuation effects have not yet been observed experimentally. On one hand, current experimental studies have focussed on the behaviour of an ensemble of droplets or micelles instead of analysing the dynamics inside an individual compartment. Individual micelles ($V \approx [10^{-21} - 10^{-23}]$ L) are moreover not stable outside the microemulsion environment and it is thus not possible to analyse their intrinsic chemical behaviour. On the other hand, our simulations showed that fluctuation effects tend to disappear for droplets with a volume larger than 10^{-12} L, which is the case for the droplets used so far in the microfluidic experiments ($V \approx [5 \times 10^{-10} - 10^{-9}]$ L).

Nevertheless, the synthesis of droplets of intermediate size ($V \approx [5 \times 10^{-18} - 10^{-12}]$ L),

matching the volumes used in our simulations, is technically feasible. Due to the limitations imposed by light microscopy, the detection of the oxidation state of such small droplets should then rely on a change in fluorescence instead of a change in absorbance. In the future, such an experimental setup could be developed to verify the theoretical predictions made *via* the model. More generally, the two fluctuation-induced phenomena identified *via* these simulations could also be exploited to design and control micro-oscillators with specific frequencies.

Acknowledgements

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