Supporting Information

Synchronization of chemical micro-oscillators

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Methods

Fabrication of the microfluidics for the controlled production of aqueous BZ microdrops was done in two ways. Either using the simple epoxy/glass based microfluidic T-junctions described elsewhere[1], or using standard soft lithographic methods to produce PDMS based devices for droplet generation. In all experiments reported here, we use a fluorinated oil, 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-trifluoromethyl-hexane (HFE 7500, 3M Corp., St. Paul, MN, USA). EA fluorinated surfactant (RainDance Technologies, Lexington, MA, USA) (2% by volume), which is a PEG-PFPE amphiphilic block copolymer,[2] was added to prevent the coalescence of water drops, particularly important in the in 1.5D and 2D geometries, where drops are nearly in contact.

The 1D and 1.5D experiments were carried out in glass capillary tubes, typically with 150 μm inner diameter. For the 2D experiments, drops produced in the microfluidic device were transferred to a standard microscope slide and then covered by another glass plate. A gasket approximately 75 μm thick placed on the slide ensured that the two plates were evenly separated.

In one series of experiments, a small amount of oil evaporated into the space between the glass plates and the gasket, squeezing the BZ drops into a smaller volume and causing them to pack tightly into a hexagonal lattice shown in Fig. 3a. In other experiments (Fig. 4), the array of drops was completely isolated from the air, also giving a hexagonal lattice, but with a larger distance between drops.

The Ru(bipy)$_3$-catalyzed BZ reaction is quite photosensitive. Illumination with 450 nm light generates bromide, which inhibits the oscillation. By subjecting the entire array of drops to homogeneous illumination at this wavelength, one can bring all the micro-oscillators into a reduced stationary state. After the illumination is removed, the drops recover their ability to oscillate and exhibit a simultaneous flash of oxidation. Thus, we can achieve an initial phase synchronization of an entire array of oscillators.

To test the hypothesis that molecular bromine serves as the inter-drop messenger, we added the surfactant Span80 (sorbitan mono-oleate) at concentrations of 5% to the oil between the BZ drops. In a separate set of experiments, we found that Span80, which has an unsaturated double bond in its hydrocarbon tail, consumes bromine in oil in less than 1 s. The water-insoluble Span80 thus acts as a trap for bromine, removing it from the oil phase.

Modeling

The most faithful way to simulate the problem is to use a detailed mechanism of the BZ reaction, such as the Field-Kőrös-Noyes (FKN) mechanism,[3] and incorporate it into partial differential equations (PDEs) with boundary conditions appropriate to the drop-oil interface and with a representative number of drops, perhaps hundreds. We might call such a model the full PDE model. However such an approach is not feasible, both because of the difficulties in characterizing the boundaries and because of the inordinate amount of computer time that would be required for the simulations.

Two methods suggest themselves for simplifying the task. First, we can eliminate all interfaces between the aqueous and oil phases, set the diffusion coefficients of the water-soluble species to zero (since they cannot diffuse outside a drop) and those of the oil soluble-molecules (Br_2 and $BrO_2^\bullet$) to a constant value D ($\cong 10^{-5}$ cm^2/s). In such a way we obtain a homogeneous simplified reaction-diffusion (SRD) model similar to that employed to describe the BZ-AOT microemulsion system.[4]

Alternatively, we can replace the diffusion process that links drops to one another through the oil gaps by simple monomolecular reactions whose rates depend on the average separation between neighboring drops. In this way, we obtain ordinary differential equations (ODEs) that can take into account a specific drop arrangement. Such ODEs should have all the solutions of the corresponding SRD model and may have additional solutions as well,[5] some of which may be artifacts that do not appear in the full PDE system. Here we focus on those solutions of the ODE model that correspond to our experimental results.

In our ODEs, we use the same FKN model[3] as in our previous work,[1] namely

$$dx/dt = - k_1xy + k_2y - 2k_3x^2 - k_4x + k_rw^2 + k_{red}wc \qquad (S1)$$

$$dy/dt = - k_1xy - k_2y - k_5yp + k_6u + k_7u + k_9z \qquad (S2)$$

$$dz/dt = k_{red}wc - k_9z - k_{10}z \qquad (S3)$$

$$dp/dt = 2k_1xy + k_2y + k_3x^2 - k_5yp + k_6u - k_8p \qquad (S4)$$

$$du/dt = k_5yp - k_6u - k_7u \qquad (S5)$$

$$dw/dt = 2k_4x - 2k_rw^2 - k_{red}wc \qquad (S6)$$

$$dc/dt = - k_{red}wc + k_9z + k_{10}z \qquad (S7)$$

where $x = [HBrO_2]$, $y = [Br^-]$, $p = [HOBr]$, $w = [BrO_2^\bullet]$, $u = [Br_2]$, c and z are the concentrations of the reduced and oxidized forms of the catalyst, respectively, $z + c = c_0$, which is constant.

The concentrations of H^+, bromate, malonic acid ([MA] = m), and bromomalonic acid (BrMA, [BrMA] = b) are taken to be fixed and are incorporated into the rate constants. For example, the constant k_9, which characterizes the rate of the reaction *ferriin* + BrMA → *ferroin* + Br^- + *products* is given as $k_9 = k_9'b$ where b is a constant concentration, set equal to a fraction of m.

Coupling between drops occurs through the oil-soluble molecules, $[Br_2]_{oil} = s$ and $[BrO_2^{\bullet}]_{oil} = r$, and depends on the geometry. We explored several drop arrangements shown in Fig. S2, which correspond to 1D (a), 1.5D (b), and 2D (c- d) experiments. For simplicity we discuss only Br_2-coupling. For the simplest 1D case, we assign a subscript n to each of the concentration variables in eqs. (S1-S7) to specify the drop in which that concentration is measured, augment eq. (S5) with pseudo-diffusion terms to obtain eq. (S8), and add a new equation (S9) for s

$$du_n/dt = k_5 y_n p_n - k_6 u_n - k_7 u_n + k_b(s_{n-1,n} + s_{n,n+1})/\rho_V - 2k_f u_n \tag{S8}$$

$$ds_{n,n+1}/dt = \rho_V k_f u_n - 2k_b s_{n,n+1} + \rho_V k_f u_{n+1} \tag{S9}$$

where $s_{n,n+1}$ denotes $[Br_2]_{oil}$ between drops n and n+1, $k_f \cong D/l^2$, D is the diffusion coefficient of Br_2 in oil or water, l is the linear size of a drop along the capillary, $k_f/k_b = P_B/\rho_V$, P_B is the partition coefficient for Br_2 between water and the oil used ($P_B = 2.5$), $\rho_V = V_W/V_{oil}$, V_W and V_{oil} are the total volumes of water drops and oil gaps (this value can be calculated from the geometry or simply from the ratio of flow rates for the syringes that inject the BZ solution and oil into the mixing device). The coefficient k_f gives the rate of bromine diffusion from a water drop to the neighboring oil gaps, while k_b is associated with the reverse process.

For the 1.5D case (Fig. S3), the coupling is more complex, since each drop has two close and two distant neighbors. In this case our equations are

$$du_{n+1}/dt = k_5 y_n p_{n+1} - k_6 u_{n+1} - k_7 u_{n+1} –$$

$$2(k_f + k_{fd})u_{n+1} + k_b(s_{n,n+1} + s_{n+1,n+2})/\rho_V + k_{bd}(s_{n-1,n+1} + s_{n+1,n+3})/\rho_{V2} \qquad \text{(S10)}$$

$$ds_{n,n+1}/dt = \rho_V k_f u_n - 2k_b s_{n,n+1} + \rho_V k_f u_{n+1} + k_O(-2s_{n,n+1} + \rho_{V3}s_{n-1,n+1} + \rho_{V3}s_{n,n+2}) \qquad \text{(S11)}$$

$$ds_{n,n+2}/dt = \rho_{V2}k_{fd}u_n - 2k_{bd}s_{n,n+2} + \rho_{V2}k_{fd}u_{n+2} + k_O(-2\rho_{V3}s_{n,n+2} + s_{n,n+1} + s_{n+1,n+2}) \qquad \text{(S12)}$$

where $k_{fd} = k_f/n_d$, and n_d is a geometric factor that takes into account the fact that the distance between drops n and n+2 is larger than the distance between drops n and n+1 . Alternatively, k_{fd} can be expressed as $k_f \cong D/l_d^2$, where l_d is the distance between distant drops n and n+2; $k_{bd} = \rho_{V2}k_{fd}/P_B$; ρ_{V2} and ρ_V (calculated for 1D) can differ in 1.5D, $\rho_{V3} = \rho_{V2}/\rho_V$. The coefficient k_O and the terms it multiplies in eqs. (S11) and (S12) take into account the fact that regions of oil between different neighboring drops can also exchange matter (bromine in this case). This complexity in our description of mass exchange between water drops originates from the fact that we use ODEs instead of the full PDEs.

For the 2D geometry we omit terms with coefficient k_O and take into account only mass exchange between neighboring drops, as in the 1D case, but the number of neighbors is larger (depending on the geometry). Note that for 1D, 1.5D, and the case of three drops in 2D (Fig. S2c), we use periodic boundary conditions, while for 7, 12, 16, 20, 24, and 28 drops in 2D (shown in Figs. 5c and S2), peripheral drops are not coupled to drops from the opposite side of the medium.

For a 3D octahedral configuration of 6 identical drops (this configuration gives periodic boundary conditions, 4 neighbors for each droplet, as well as a total number of drops divisible by 3), we also use only mass exchange between neighboring drops.

Results

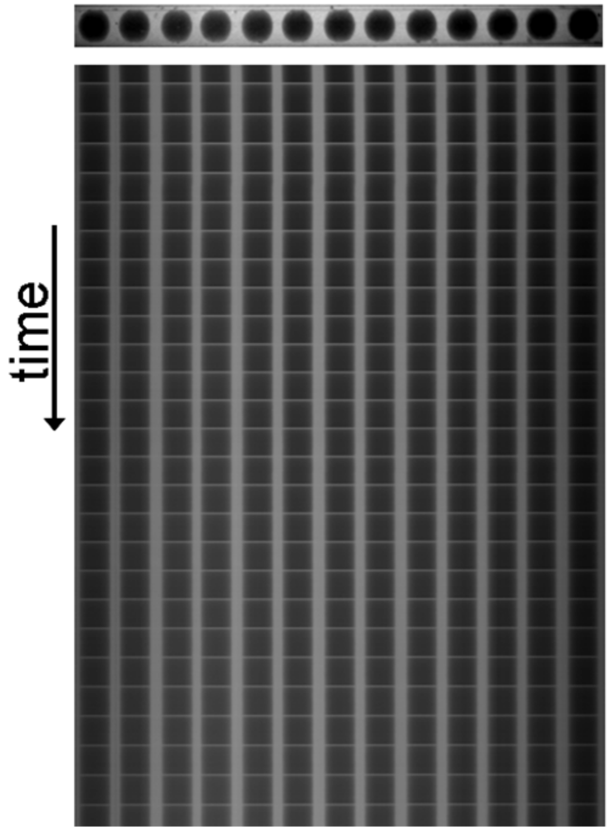

Figure S1. Glass capillary with BZ drops (top) and space-time plot of in-phase oscillations obtained experimentally. Spikes of oxidation of ferroin are seen as light horizontal lines across BZ-droplets. Horizontal length of the frame and the capillary ID are 3.8 mm and 150 µm; the total time is 5400 s. The initial concentrations of reactants: [H_2SO_4] = 80 mM, [$NaBrO_3$] = 0.288 M, [MA] = 0.64 M, [NaBr] = 10 mM, [ferroin] = 3 mM, and [$Ru(bpy)_3$] = 0.4mM (bpy=bipyridine).

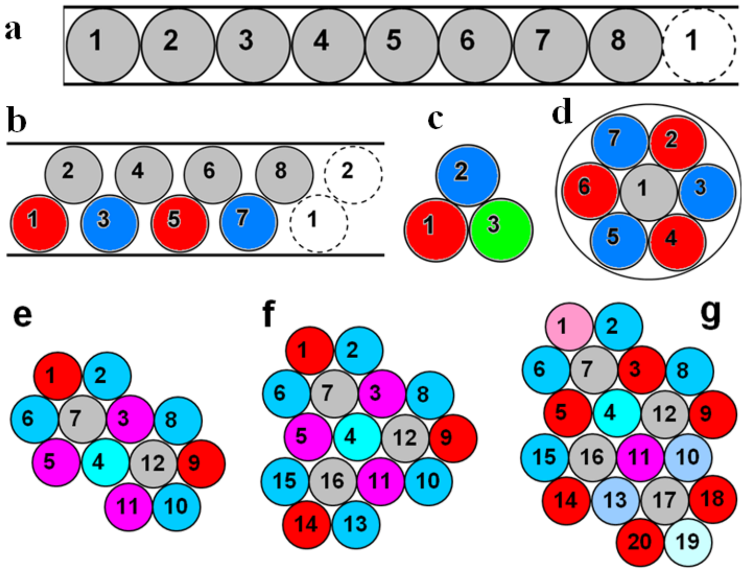

Figure S2. Drop arrangements. Oil gaps between neighboring drops are not shown. (a) 1D case, (b) 1.5D case. Both (a) and (b) have periodic boundary conditions. (c)-(g) Schematic depiction of 2D results. Gray drops are stationary in (b) – (g). Bluish (like 2, 4, 8, 10, 19 in panel g) and reddish (like 1, 3, 9, 11, 18 in panel g) drops oscillate approximately in phase with drops of the similar color and 180^{o} out of phase with drops of the other color group.

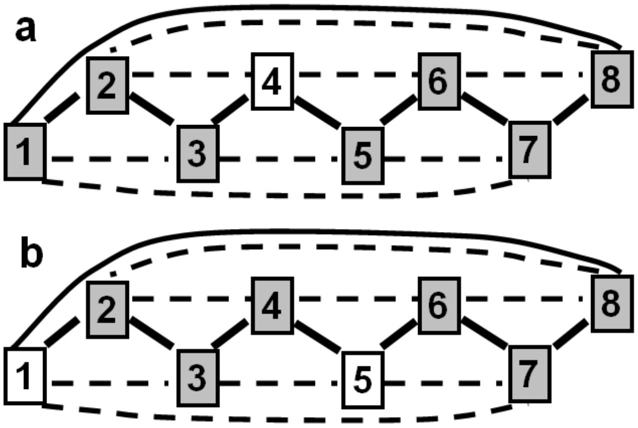

Figure S3. Stationary Turing patterns in simulations of 8 identical coupled BZ drops for 1.5 D configuration. Drop 4 in (a) and drops 1 and 5 in (b) are in the oxidized state. Parameters for the FKN model S1-S7 + S10-S12: $h = [H^+] = 0.2$ M, $a = [BrO_3^-] = 0.3$ M, $m = [MA] = 0.03$ M, $c_0 = 0.003$ M, k_f = (a) 10 s^{-1}, (b) 1 s^{-1}, $\rho_V = 10$, $k_{fd} = k_f/10$, $\rho_{V2} = 2$, $k_{bd} = \rho_{V2}k_{fd}/P_B$, $k_b = \rho_V k_f/P_B$, $k_O = k_{fr} = 0$, $k_1 = k_1'h$, $k_1' = 2 \times 10^6$ M^{-2} s^{-1}, $k_2 = k_2'h^2a$, $k_2' = 2$ M^{-3} s^{-1}, $k_3 = 3000$ M^{-1} s^{-1}, $k_4 = k_4'ha$, $k_4' = 42$ M^{-2} s^{-1}, $k_5 = k_5'h$, $k_5' = 5 \times 10^9$ M^{-2} s^{-1}, $k_6 = 10$ s^{-1}, $k_7 = k_7'm$, $k_7' = 29$ M^{-1} s^{-1}, $k_8 = k_8'm$, $k_8' = 9.3$ M^{-1} s^{-1}, $k_9 = k_9'm$, $k_9' = 0.1$ M^{-1} s^{-1}, $k_{10} = k_{10}'m$, $k_{10}' = 0.05$ M^{-1} s^{-1}, $k_r = 2 \times 10^8$ M^{-1} s^{-1}, $k_{red} = 5 \times 10^6$ M^{-1} s^{-1}, $P_B = 2.5$, $\rho_{V3} = \rho_{V2}/\rho_V$.

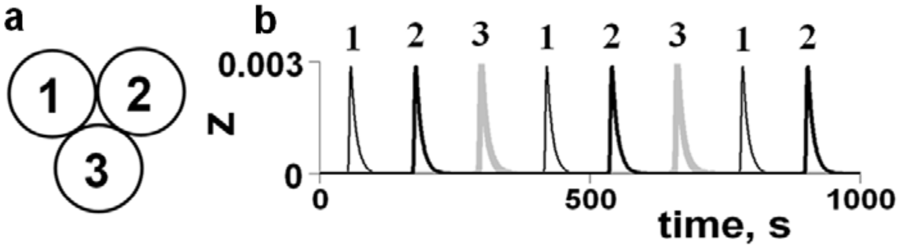

Figure S4. Simulations of three identical BZ drops (a) with $2\pi/3$ phase shifted oscillations shown in (b). Parameters of model S1-S9: $h = 0.16$ M, $a = 0.3$ M, $m = 0.65$ M, $k_f = 0.5$ s^{-1}, $\rho_V = 50$, all other constants as in Fig. S3.

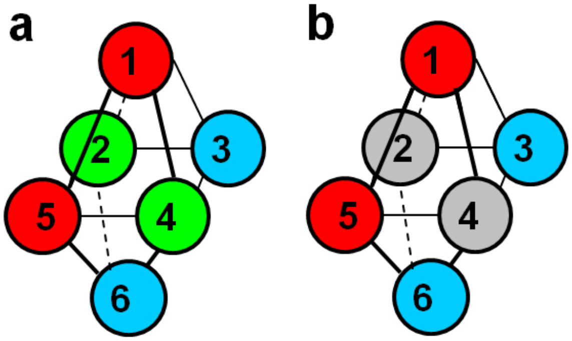

Figure S5. Simulations of six identical BZ drops with periodic boundary conditions in 3D (octahedron) (a) with 2π/3 phase shifted oscillations (drops with the same color oscillate in-phase) and (b) with stationary drops 2 and 4, while synchronously oscillating drops 1 and 5 are anti-phase to synchronously oscillating drops 3 and 6. Parameters of model S1-S9: $h = 0.16$ M, $a = 0.3$ M, $m = 0.65$ M, $\rho_V = 10$, $P_B = 2.5$, $k_f = 0.1 – 0.2$ s^{-1} for (a) and $k_f = 0.5 – 8$ s^{-1} for (b), all other constants as in Fig. S3. For $k_f = 0.4$ s^{-1} both solutions are possible. Other solutions, e.g., anti-phase oscillations (without stationary drops) are also possible for a broad range of coupling strength k_f.

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