Impact of PDMS-based Microfluidics on Belousov - Zhabotinsky Chemical Oscillators: Supplement

James Sheehy, Ian Hunter, Maria Eleni Moustaka, S. Ali Aghvami, Youssef Fahmy, and Seth Fraden*

Department of Physics, Brandeis University, Waltham, MA 02453*

E-mail: fraden@brandeis.edu

Supplement

Temperature Control

To increase experimental reproducibility, we use thermal control to keep a consistent temperature. The clamp contains two Peltier devices and a thermistor which are connected to an Arduino microcontroller (Fig. S1A). The system uses a PID control loop to maintain the temperature, which was implemented using standard Arduino libraries. Excess heat is removed from the Peltiers by use of a water pump. This allows us to keep the temperature within a fraction of a degree of our desired temperature (Fig. S1C).

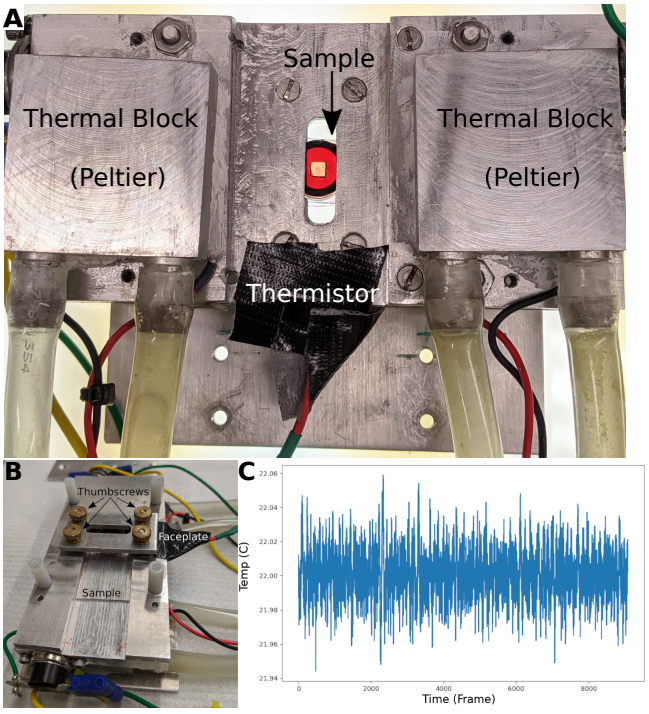

Figure S1: (A) Photograph of the temperature controlled clamp used for experiments. The sample is situated between two Peltier devices, near the thermistor. (B) Side view of temperature controlled clamp showing the sealing mechanism. The sample is sealed using thumbscrews which add pressure to the faceplate. (C) A plot of the temperature over time. The temperature stays within a tenth of a degree of the 22 C set-point throughout the entire data acquisition.

Computational Models

For all computational models, we use the Vanag-Epstein model of BZ. This model uses a four chemical representation of BZ, simulating the concentrations of $HBrO_2$ (x), Br^- (y),

oxidized catalyst (z), and Br_2 (u).

$$\frac{dx}{dt} = -k_1xy + k_2y - 2k_3x^2 + k_4\frac{x(c_0 - z)}{c_0 - z + c_{\min}}$$

$$\frac{dy}{dt} = -3k_1xy - 2k_2y - k_3x^2 + k_7u + k_9z + k(I)\frac{c_0 - z}{b_C/b + 1}$$

$$\frac{dz}{dt} = 2k_4\frac{x(c_0 - z)}{c_0 - z + c_{min}} - k_9z - k_{10}z + k(I)\frac{c_0 - z}{b_C/b + 1}$$

$$\frac{du}{dt} = 2k_1xy + k_2y + k_3x^2 - k_7u$$

The parameters for the model are as follows The photogeneration rate, k(I), is a parameter

Table S1: Vanag-Epstein Model Parameters

Parameter/ Rate	Value	Unit
h	.16	M
a	.288	M
m	.4	M
b	.12 m	M
c_0	.0042	M
b_c	.05	M
c_{min}	$6.1*10^{-5}$	M
k_1	$2*10^6$h	M^{-1} s^{-1}
k_2	$2h^2a$	s^{-1}
k_3	$3*10^3$	M^{-1} s^{-1}
k_4	42 h a	$M^{-1}s^{-1}$
k_7	29 m	s^{-1}
k_9	.12 m	s^{-1}
k_{10}	.05 m	s^{-1}
P	2.5	
D_0	1000	μm^2 s^{-1}
f	.15	

which we can set to mimic the effects of light. For interpreting our model, we assume that k(I) is proportional to the intensity.

PDMS Thickness Model

We create an idealized reaction-diffusion model consisting of 3 points to model the experimental system of a BZ filled well (B) fabricated out of PDMS (S) and surrounded by a moat (M). We label each of the chemicals in the region using a subscript, with the subscripts M, B, and S representing the moat, BZ, and the PDMS respectively. Each point is governed by a set of reactions and diffusive coupling with neighbors. The depth of the moat and the well, (d), is simulated with a thickness of 30 µm. The PDMS is simulated using a variable thickness, L. Both the BZ and moat are simulated using the VE model, with the BZ simulated using a k(I)=0 s^{-1}, and the moat simulated using a k(I)= 10^{-4} s^{-1}. We assume that only the non-polar molecule bromine permeates from the aqueous BZ solution into the PDMS. We further assume that bromine reacts with some unknown reactant within the PDMS that is present at an unknown concentration. Furthermore, we assume that the concentration of the reactant is large enough that it can be considered constant. With these assumptions, the reaction within the PDMS takes the form:

$$\frac{du_{\mathrm{S}}}{dt} = -k * u_{\mathrm{S}}$$

The reaction rate between the PDMS and bromine, k, is left as a fitting parameter.

We can therefore write the reaction-diffusion equations for the chemicals within each domain as:

$$\frac{dx_{\mathrm{B}}}{dt} = -k_1 x_{\mathrm{B}} y_{\mathrm{B}} + k_2 y_{\mathrm{B}} - 2k_3 x_{\mathrm{B}}^2 + k_4 \frac{x(c_0 - z_{\mathrm{B}})}{c_0 - z_{\mathrm{B}} + c_{\mathrm{min}}}$$

$$\frac{dy_{\mathrm{B}}}{dt} = -3k_1 x_{\mathrm{B}} y_{\mathrm{B}} - 2k_2 y_{\mathrm{B}} - k_3 x_{\mathrm{B}}^2 + k_7 u_{\mathrm{B}} + k_9 z_{\mathrm{B}}$$

$$\frac{dz_{\mathrm{B}}}{dt} = 2k_4 \frac{x_{\mathrm{B}}(c_0 - z_{\mathrm{B}})}{c_0 - z_{\mathrm{B}} + c_{\mathrm{min}}} - k_9 z_{\mathrm{B}} - k_{10} z_{\mathrm{B}}$$

$$\frac{du_{\mathrm{B}}}{dt} = 2k_1 x_{\mathrm{B}} y_{\mathrm{B}} + k_2 y_{\mathrm{B}} + k_3 x_{\mathrm{B}}^2 - k_7 u_{\mathrm{B}} + \mu_{SB}(u_S - P * u_B)$$

$$\frac{du_{\mathrm{S}}}{dt} = -k * u_{\mathrm{S}} + \mu_{BS}(P * u_B - u_S) + \mu_{MS}(P * u_M - u_S)$$

$$\frac{dx_{\mathrm{M}}}{dt} = -k_1 x_{\mathrm{M}} y_{\mathrm{M}} + k_2 y_{\mathrm{M}} - 2k_3 x_{\mathrm{M}}^2 + k_4 \frac{x_{\mathrm{M}}(c_0 - z_{\mathrm{M}})}{c_0 - z_{\mathrm{M}} + c_{\mathrm{min}}}$$

$$\frac{dy_{\mathrm{M}}}{dt} = -3k_1 x_{\mathrm{M}} y_{\mathrm{M}} - 2k_2 y - k_3 x_{\mathrm{M}}^2 + k_7 u + k_9 z_{\mathrm{M}} + k(I)\frac{c_0 - z_{\mathrm{M}}}{b_{\mathrm{C}}/b + 1}$$

$$\frac{dz_{\mathrm{M}}}{dt} = 2k_4 \frac{x(c_0 - z)}{c_0 - z_{\mathrm{M}} + c_{\mathrm{min}}} - k_9 z - k_{10} z_{\mathrm{M}} + k(I)\frac{c_0 - z_{\mathrm{M}}}{b_{\mathrm{C}}/b + 1}$$

$$\frac{du_{\mathrm{M}}}{dt} = 2k_1 x_{\mathrm{M}} y_{\mathrm{M}} + k_2 y_{\mathrm{M}} + k_3 x_{\mathrm{M}}^2 - k_7 u_{\mathrm{M}} + \mu_{SM}(u_S - P * u_M)$$

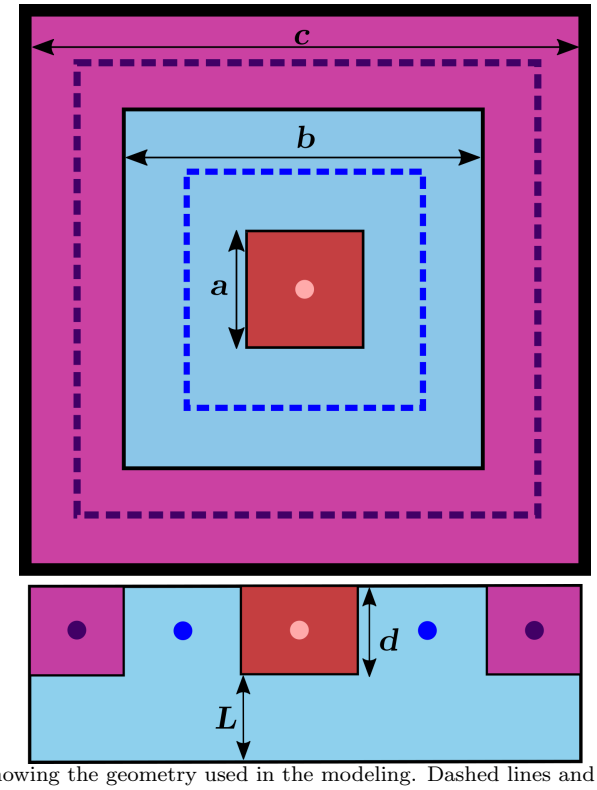

Figure S2: A labeled diagram showing the geometry used in the modeling. Dashed lines and dot represent the points modeled in the simulation, as sampled from the middle of the domains. For these experiments, $a = 120$ µm, $b = 632$ µm, $c = 840$ µm, and $d = 30$ µm. The thickness, L, is variable.

To model the diffusive bromine flux between the elements in our simulation, we use the method provided by Norton et. al.[1] The flux of a chemical c at points i due to a concentration difference with point j is given as: $\frac{dc_i}{dt} = \mu_{\mathrm{ji}} * (c_{\mathrm{j}} - c_{\mathrm{i}})$. The quantity, μ_{ji}, can be thought of

as the coupling strength between two domains containing BZ. It has units of 1/sec and can also be considered a diffusive rate that is analogous to a reaction rate in first order chemical kinetics, given as:

$$\mu_{\mathrm{ji}} = \frac{PD_0 f A_{\mathrm{ji}}}{l_{\mathrm{ji}} V_{\mathrm{i}}}$$

P is the partition coefficient, D_0 is the diffusion coefficient, and f is a fitting factor. The product PD_0f is the effective diffusion constant of bromine in PDMS which we call D. This quantity has not been measured. However, an estimate for the effective diffusion constant of bromine in fluorinated oil is $D = 375$ µm^{2}s^{-1}.[1]

The system we use for the model is shown in Fig S2. Each of the points modeled in our simulation is represented at the midpoint of each of the domains. We define the distance a as the size of the well the distance b as the size of the PDMS domain encapsulated by the moat, and the distance c as the end to end distance of the moat. For the experimental setup we used, $a = 120$ µm, $b = 632$ µm , and $c = 840$ µm. Additionally, the thickness of the features, $d = 30$ µm, while the PDMS thickness L varies.

The variable V_i represents the volume of the element receiving the flux, A_{ji} is the cross sectional area of the coupled elements, and l_{ji} is the separation between the elements. The geometric parameters used are shown in the table below. For the total volume of PDMS, we consider the volume of the PDMS directly under the BZ well, as well as the PDMS between the BZ well and moat. All lengths are the distances between the midpoints of the domains.

Table S2: PDMS Thickness Model Sizes

l_{BS} =	$\frac{b+a}{4}$ =	188	µm
l_{SM} =	$\frac{c-a}{4}$ =	180	µm
A_{BS} =	$4(a*d)+a^2$ =	2.88*10^4	µm^2
A_{SM} =	$(c^2-b^2)+4*(b*d)$ =	3.82*10^5	µm^2
V_B =	a^2*d =	4.32*10^6	µm^3
V_S =	$c^2*L+(b^2-a^2)*d$ =	7*10^{5}L+1.16*10^7	µm^3
V_M =	$(c^2-b^2)d$ =	9.19*10^6	µm^3

Using the experimental geometry, we calculated the values of the various μ_{ji}, summarized in the table below. To simulate the coupling, we used the experimental geometry to calculate

the coupling constants between the BZ and the PDMS (μ_{BS}), the PDMS and the BZ (μ_{SB}), the moat and the PDMS(μ_{MS}), and the PDMS and the moat(μ_{SM}). For a system with a PDMS thickness of L, the coupling constants are as follows:

Table S3: PDMS Thickness Coupling Constants

$\mu_{BS} =$	$\frac{DA_{BS}}{l_{BS}V_S} =$	$\frac{375*2.88*10^4}{188*(7*10^5L+1.16*10^7)} =$	$\frac{5.74}{7*10L+116}\ s^{-1}$
$\mu_{SB} =$	$\frac{DA_{BS}}{l_{BS}V_B} =$	$\frac{375*2.88*10^4}{188*(4.32*10^6)} =$	$1.33*10^{-1}s^{-1}$
$\mu_{MS} =$	$\frac{DA_{SM}}{l_{SM}V_S} =$	$\frac{375*3.8*10^5}{180*(7*10^5L+1.16*10^7)} =$	$\frac{7.92}{7*10L+116}s^{-1}$
$\mu_{SM} =$	$\frac{DA_{SM}}{l_{SM}V_M} =$	$\frac{375*3.8*10^5}{180*9.19*10^6} =$	$8.61*10^{-2}\ s^{-1}$

Light Phase Response Curve

To simulate the phase response curve of BZ when perturbed with light, we once again use the VE simulations. To mimic applying an intense light to the wells, we increase the k(I) term in order to perturb the system. We then restore the k(I) term to zero and measure the time to the next BZ oscillation. We compare the difference in times between the two oscillations to ascertain the effect of the perturbation. To match the intensity that we use in the experiments, we chose a k(I) that yielded the best agreement between theory and experiment for the 3 second phase response curve exposure. For these simulations our measured best fit for k(I)/k(I_c) was 3.63.

Supplementary Movie

Movie S1: A movie showing four oscillating BZ wells surrounded by moats. The movie has been sped up by a factor of 160 and the wells sit atop a 2 µm thick layer of PDMS. Oscillations in the moats are suppressed by the application of light from a computer projector. However, the light from the computer projector is only shone onto the sample when the camera is not recording images. Therefore one never sees the moat illuminated in the video.

References

(1) Norton, M. M.; Tompkins, N.; Blanc, B.; Cambria, M. C.; Held, J.; Fraden, S. Dynamics of Reaction-Diffusion Oscillators in Star and other Networks with Cyclic Symmetries Exhibiting Multiple Clusters. *Physical review letters* **2019**, *123*, 148301.