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

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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 \( \text{Br}_2 \) \( (u) \).

\[
\frac{dx}{dt} = -k_1 xy + k_2 y - 2k_3 x^2 + k_4 \frac{x(c_0 - z)}{c_0 - z + c_{\text{min}}}
\]

\[
\frac{dy}{dt} = -3k_1 xy - 2k_2 y - k_3 x^2 + k_7 u + k_9 z + k(I) \frac{c_0 - z}{b c/b + 1}
\]

\[
\frac{dz}{dt} = 2k_4 \frac{x(c_0 - z)}{c_0 - z + c_{\text{min}}} - k_9 z - k_{10} z + k(I) \frac{c_0 - z}{b c/b + 1}
\]

\[
\frac{du}{dt} = 2k_1 xy + k_2 y + k_3 x^2 - k_7 u
\]

The parameters for the model are as follows:

<table>
<thead>
<tr>
<th>Parameter/ Rate</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( h )</td>
<td>.16</td>
<td>M</td>
</tr>
<tr>
<td>( a )</td>
<td>.288</td>
<td>M</td>
</tr>
<tr>
<td>( m )</td>
<td>.4</td>
<td>M</td>
</tr>
<tr>
<td>( b )</td>
<td>.12 m</td>
<td>M</td>
</tr>
<tr>
<td>( c_0 )</td>
<td>.0042</td>
<td>M</td>
</tr>
<tr>
<td>( b_c )</td>
<td>.05</td>
<td>M</td>
</tr>
<tr>
<td>( c_{\text{min}} )</td>
<td>6.1*10^{-5}</td>
<td>M</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>2*10^6h</td>
<td>M^{-1} s^{-1}</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>2h^2a</td>
<td>s^{-1}</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>3*10^3</td>
<td>M^{-1} s^{-1}</td>
</tr>
<tr>
<td>( k_4 )</td>
<td>42 h a</td>
<td>M^{-1} s^{-1}</td>
</tr>
<tr>
<td>( k_7 )</td>
<td>29 m</td>
<td>s^{-1}</td>
</tr>
<tr>
<td>( k_9 )</td>
<td>.12 m</td>
<td>s^{-1}</td>
</tr>
<tr>
<td>( k_{10} )</td>
<td>.05 m</td>
<td>s^{-1}</td>
</tr>
<tr>
<td>( P )</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>( D_0 )</td>
<td>1000</td>
<td>\mu m^2 s^{-1}</td>
</tr>
<tr>
<td>( f )</td>
<td>.15</td>
<td></td>
</tr>
</tbody>
</table>

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 \( \mu \text{m} \). 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 \( k(I) = 0 \ \text{s}^{-1} \), and the moat simulated using a \( k(I) = 10^{-4} \ \text{s}^{-1} \). 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:

\[
\frac{du_S}{dt} = -k * u_S
\]

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:

\[
\begin{align*}
\frac{dx_B}{dt} &= -k_1 x_B y_B + k_2 y_B - 2k_3 x_B^2 + k_4 \frac{x(c_0 - z_B)}{c_0 - z_B + c_{\text{min}}} \\
\frac{dy_B}{dt} &= -3k_1 x_B y_B - 2k_2 y_B - k_3 x_B^2 + k_7 u_B + k_9 z_B \\
\frac{dz_B}{dt} &= k_4 \frac{x_B(c_0 - z_B)}{c_0 - z_B + c_{\text{min}}} - k_9 z_B - k_{10} z_B \\
\frac{du_B}{dt} &= 2k_1 x_B y_B + k_2 y_B + k_3 x_B^2 - k_7 u_B + \mu_{SB}(u_S - P * u_B)
\end{align*}
\]
\[
\frac{du_S}{dt} = -k * u_S + \mu_{BS}(P * u_B - u_S) + \mu_{MS}(P * u_M - u_S)
\]

\[
\frac{dx_M}{dt} = -k_1 x_M y_M + k_2 y_M - 2k_3 x_M^2 + k_4 \frac{x_M (c_0 - z_M)}{c_0 - z_M + c_{\text{min}}}
\]

\[
\frac{dy_M}{dt} = -3k_1 x_M y_M - 2k_2 y - k_3 x_M^2 + k_7 u + k_9 z_M + k(I) \frac{c_0 - z_M}{b_C/b + 1}
\]

\[
\frac{dz_M}{dt} = 2k_4 \frac{x (c_0 - z)}{c_0 - z_M + c_{\text{min}}} - k_9 z - k_{10} z_M + k(I) \frac{c_0 - z_M}{b_C/b + 1}
\]

\[
\frac{du_M}{dt} = 2k_1 x_M y_M + k_2 y_M + k_3 x_M^2 - k_7 u_M + \mu_{SM}(u_S - P * u_M)
\]

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, \(a = 120 \, \mu m\), \(b = 632 \, \mu m\), \(c = 840 \, \mu m\), and \(d = 30 \, \mu m\). 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: \[
\frac{dc_i}{dt} = \mu_{ji} \ast (c_j - c_i).
\] The quantity, \(\mu_{ji}\), 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:

$$\mu_{ji} = \frac{PD_0fA_{ji}}{l_{ji}V_i}$$

$P$ 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 $D = 375 \mu m^2 s^{-1}$.\(^1\)

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, $a = 120 \mu m$, $b = 632 \mu m$, and $c = 840 \mu m$. Additionally, the thickness of the features, $d = 30 \mu m$, 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>
<thead>
<tr>
<th>Table S2: PDMS Thickness Model Sizes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_{BS} = \frac{b+a}{4} = 188 \mu m$</td>
</tr>
<tr>
<td>$l_{SM} = \frac{c-a}{4} = 180 \mu m$</td>
</tr>
<tr>
<td>$A_{BS} = 4(a * d) + a^2 = 2.88*10^4 \mu m^2$</td>
</tr>
<tr>
<td>$A_{SM} = (c^2 - b^2) + 4 * (b * d) = 3.82*10^5 \mu m^2$</td>
</tr>
<tr>
<td>$V_B = a^2 * d = 4.32*10^6 \mu m^3$</td>
</tr>
<tr>
<td>$V_S = c^2 * L + (b^2 - a^2) * d = 7<em>10^7 L + 1.16</em>10^7 \mu m^3$</td>
</tr>
<tr>
<td>$V_M = (c^2 - b^2)d = 9.19*10^6 \mu m^3$</td>
</tr>
</tbody>
</table>

Using the experimental geometry, we calculated the values of the various $\mu_{ji}$, 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 ($\mu_{BS}$), the PDMS and the BZ ($\mu_{SB}$),
the moat and the PDMS($\mu_{MS}$), and the PDMS and the moat($\mu_{SM}$). For a system with a
PDMS thickness of $L$, the coupling constants are as follows:

<table>
<thead>
<tr>
<th>Coupling Constant</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{BS}$</td>
<td>$\frac{DA_{BS}}{l_{BS}v_S} = \frac{375 \times 2.88 \times 10^4}{188(7 \times 10^9 L + 1.16 \times 10^7)} = \frac{5.74}{7 \times 10^7 + 116} s^{-1}$</td>
</tr>
<tr>
<td>$\mu_{SB}$</td>
<td>$\frac{DA_{BS}}{l_{BS}v_B} = \frac{375 \times 2.88 \times 10^4}{188(4.32 \times 10^6)} = 1.33 \times 10^{-1}s^{-1}$</td>
</tr>
<tr>
<td>$\mu_{MS}$</td>
<td>$\frac{DA_{SM}}{l_{SM}v_S} = \frac{375 \times 3.8 \times 10^5}{180(7 \times 10^9 L + 1.16 \times 10^7)} = \frac{7.92}{7 \times 10^7 + 116}s^{-1}$</td>
</tr>
<tr>
<td>$\mu_{SM}$</td>
<td>$\frac{DA_{SM}}{l_{SM}v_M} = \frac{375 \times 3.8 \times 10^5}{180 \times 9.19 \times 10^6} = 8.61 \times 10^{-2}s^{-1}$</td>
</tr>
</tbody>
</table>

**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