Supporting Online Material for

Dynamical Quorum Sensing and Synchronization in Large Populations of Chemical Oscillators

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Materials and Methods

1. Particles

The preparation of microporous cation-exchange beads (DOWEX 50WX4-200) with ferroin catalyst ([Fe(phen)]^{2+} = 1.7 \times 10^{-5} \text{ M}) is described in Ref. (13). Particles have a distribution of sizes (Fig. S1a) and variations in catalyst loading as a result of varying available ion exchange sites. Particles therefore display a broad range of oscillatory frequencies (Fig. S1b) when placed in unstirred catalyst-free Belousov-Zhabotinsky (BZ) solutions. The number density $n$ of particles is estimated from $n = N/V_s = V_p/\bar{V}_s$, where $N$ is the total number of particles, $V_p$ is the volume occupied by wet particles in solution (calculated as $V_p = 5V_d$, where $V_d$ is the volume displacement of dry particles, to account for the 80% solution absorption of the particles), $V_s$ is the total volume of solution and $\bar{V}$ is the average volume of a particle (calculated from $\bar{r} = 120 \mu\text{m}$). When a mass of 0.2 g of dry particles is added to 10.0 cm$^3$ of solution, the volume displacement is 0.17 cm$^3$, and the number of particles $N$ is $1.2 \times 10^5$ and $n = 1.2 \times 10^4 \text{ cm}^{-3}$.

2. Experimental set-up

The reactor is a closed cylindrical vessel of diameter 1.8 cm filled with 10.0 cm$^3$ of catalyst-free BZ reaction solution ([NaBr] = 0.07 M, [MA] = 0.14 M, [NaBrO$_3$] = 0.49 M, [H$_2$SO$_4$] = 0.67 M) and thermostated at a temperature of 20.0 °C. The concentrations of species in solution are followed with a redox microelectrode (MI-800). The reactor is fitted with a viewing window and screen for imaging and illuminated with two fiber-optic lamps. Images are obtained with a digital camera (Insight IN1120) with a shutter speed of 0.4 ms. The particles have high velocities in the stirred suspension and consecutive images therefore contain different sets of particles. Stirring is achieved using a magnetic stirrer (IKAMAG) and a bar of length 1.7 cm or an overhead stirrer with 4 paddles constructed in-house. The experimental results presented in this work are qualitatively reproducible with a change in the method of stirring. The transitions occurred at lower stirring rates with the motor-driven impeller, suggesting that the exchange rate for a particular stirring rate is higher with the motor-driven impeller than with the magnetic stirring bar. The stirring rate is varied between 100 and 700 rpm. Particles are completely suspended in the solution. The procedure for increasing the particle density involved the addition of a known amount of dry catalyst particles to the stirred solution.
3. Numerical simulations

Simulations exploit the ZBKE model of the BZ reaction (17), with the rate of change of variables HBrO$_2$ ($X$), Br$^-$ ($Y$) and oxidized form of the catalyst ($Z$) for $i = 1, \ldots N$ particles given by:

$$\frac{dX_i}{dt} = -k_{ex}(X_i - X_s) - k_2 h_0 X_i Y_i + k_3 h_0 A Y_i - 2k_4 X_i^2 - k_5 h_0 A X_i + k_{-5} U_{ss} + k_6 U_{ss} (C - Z_i) - k_{-6} X_i Z_i$$

$$\frac{dY_i}{dt} = -k_{ex}(Y_i - Y_s) - k_2 h_0 X_i Y_i - k_3 h_0 A Y_i + q_i \frac{k_1 k_9 BZ_i}{k_{-7} h_0 (C - Z_i) + k_8} + k_9 B$$

$$\frac{dZ_i}{dt} = k_6 U_{ss} (C - Z_i) - k_{-6} X_i Z_i - \frac{k_1 k_9 BZ_i}{k_{-7} h_0 (C - Z_i) + k_8}$$

and in the surrounding solution:

$$\frac{dX_s}{dt} = \frac{\bar{V}}{V_s} \sum_{i=1}^{N} k_{ex}(X_i - X_s) - k_2 h_0 X_s Y_s + k_3 h_0 A Y_s - 2k_4 X_s^2 + k_{-5} U_{ss}^2$$

$$\frac{dY_s}{dt} = \frac{\bar{V}}{V_s} \sum_{i=1}^{N} k_{ex}(Y_i - Y_s) - k_2 h_0 X_s Y_s - k_3 h_0 A Y_s + k_9 B$$

where $A = [\text{HBrO}_3]$, $B = [\text{BrMA} + \text{MA}]$, $C = \text{total catalyst}$, $h_0 = \text{acidity}$, $q_i = \text{stoichiometric coefficient}$, $k_2 - k_9 = \text{rate constants}$, $k_{ex} = \text{exchange rate constant}$, $\bar{V} = \text{average volume of a particle}$, $V_s = \text{volume of solution}$, and the value of HBrO$_2^+$ ($U$) is obtained via its steady state concentration:

$$U_{ss} = \frac{1}{4k_{-5}} (-k_6 (C - Z_i) + (k_6^2 (C - Z_i)^2 + 16k_{-5} k_9 h_0 A X_i + 8k_{-5} k_{-6} X_i Z_i)^{\frac{1}{2}}$$

The parameter values are listed in Table S1. Note that for the surrounding solution, $X_i = X_s$, $C = 0$ and $Z_i = 0$ in the expression for $U_{ss}$. The model treats the particles as homogeneous spherical reactors of average volume $\bar{V}$, and the exchange of species occurs from the surface to the surrounding solution. Following previous work (13), the numerical results are presented for particles with a range of frequencies determined from a Gaussian distribution in the stoichiometric coefficient $q$. The frequency distribution may also be obtained with a distribution in catalyst concentration or particle size, and qualitatively similar results are observed.
Supporting Text

1. Effect of stirring rate on the chemical exchange rate

The transfer of species $X$ from a catalyst particle to the surrounding solution is considered as a “reversible surface reaction” (Ref. S1): $X_{\text{particle}} \leftrightarrow X_{\text{solution}}$. The rate at which $X$ is transferred from the particle to the surrounding solution is given by $-k_{\text{ex}}(X_i - X_s)$ where $X_i$ is the concentration on the particle, $X_s$ is the concentration in the solution, and the exchange rate constant $k_{\text{ex}}$ is equal to $k_{\text{sl}}A/V$, where $A$ is the surface area of the particle, $V$ is the volume of the particle, and $k_{\text{sl}}$ is the solid to liquid mass transfer coefficient. In the absence of stirring, $k_{\text{sl}}$ is related to the diffusion coefficient of $X$ in solution ($\sim D/\delta$ where $\delta$ is the thickness of the boundary layer separating the particle and the solution). In stirred suspensions, $k_{\text{sl}}$ depends on the method of stirring as well as the stirring rate. There is no simple expression for $k_{\text{sl}}$ but experimentally determined values generally range between $10^{-3}$ and $10^{-1}$ cm s$^{-1}$ for catalytic microparticles and the value of $k_{\text{sl}}$ increases monotonically with increasing stirring rate (Ref. S2). The experimental results are replicated by the model assuming that the surrounding solution is well mixed and $k_{\text{sl}}$ varies between $10^{-3}$ cm s$^{-1}$ and $10^{-2}$ cm s$^{-1}$.

2. Influence of the heterogeneity on the dynamical transitions

Coupling by the exchange of signalling species with the surrounding solution provides a means for the population to behave as a coherent whole despite its natural heterogeneity. In Fig. S2a, the order parameter $K$ is plotted for heterogeneous (black line) and homogeneous (colored lines) populations with increasing $k_{\text{ex}}$ and fixed $n$. The growth in $K$ with $k_{\text{ex}}$ in the heterogeneous population ($q = 0.6 \pm 0.05$) corresponds to the synchronization of the oscillators. The sharp drop to $K = 0$ is associated with the simultaneous cessation of oscillatory activity on all particles. The critical value of $k_{\text{ex}}$ is $1.2$ s$^{-1}$ for the heterogeneous population and ranges between $0.7$ s$^{-1}$ and $1.4$ s$^{-1}$ for the homogeneous populations with the indicated values of $q$ and associated periods. The transition from quiescence to synchronized oscillatory activity with increasing $n$ at high exchange rate is shown in Fig. S2b. The value of $K$ switches from 0 to 1 at a critical $n$ with the onset of synchronized oscillations on all particles. In the heterogeneous population, all particles oscillate synchronously for $n_{\text{crit}} = 7.0 \times 10^4$ cm$^{-3}$. The transition to synchronous oscillatory behavior in the homogeneous populations occurs between $n_{\text{crit}} = 4.8 \times 10^4$ cm$^{-3}$ and $12.1 \times 10^4$ cm$^{-3}$ depending on the value of $q$. Note that the values of $n_{\text{crit}}$ are nearly the same for the heterogeneous population and the homogeneous population with $q = 0.6.$
Supporting Figures

Fig. S1. Typical distribution in catalytic particle (a) radii and (b) oscillatory period in unstirred BZ solutions. The period of non-interacting particles was measured for (b). (Measurements by A. F. Taylor and R. Toth.)

Fig. S2. Influence of heterogeneity on the model transitions with increasing \( k_{\text{ex}} \) and \( n \). Order parameter \( K \) for identical oscillators (colored lines) and for heterogeneous population of oscillators (black line) with (a) increasing \( k_{\text{ex}} \) \((n = 1.8 \times 10^4 \text{ cm}^{-3})\) and (b) increasing \( n \) \((k_{\text{ex}} = 3.0 \text{ s}^{-1})\). Histograms of oscillator periods (unstirred conditions: \( k_{\text{ex}} = 0.03 \text{ s}^{-1} \)) with corresponding values of the stoichiometric coefficient \( q \) are shown on the right.
Supporting Tables

Table S1. The values of parameters in the model

<table>
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<th>Parameter</th>
<th>$A$ (M)</th>
<th>$B$ (M)</th>
<th>$C$ (M)</th>
<th>$h_0$ (M)</th>
<th>$\overline{q}$</th>
<th>$\sigma_\overline{q}$</th>
<th>$k_2$ (M$^2$ s$^{-1}$)</th>
<th>$k_3$ (M$^2$ s$^{-1}$)</th>
<th>$k_4$ (M$^{-1}$ s$^{-1}$)</th>
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<tr>
<td>Value</td>
<td>0.39</td>
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<td>0.05</td>
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<td>Parameter</td>
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<td>$k_5$ (M$^{-1}$ s$^{-1}$)</td>
<td>$k_6$ (M$^{-1}$ s$^{-1}$)</td>
<td>$k_6$ (M$^{-1}$ s$^{-1}$)</td>
<td>$k_8/k_7$ (M$^{-1}$ s$^{-1}$)</td>
<td>$k_8k_7/k_7$ (M$^{-1}$ s$^{-1}$)</td>
<td>$k_9$ (s$^{-1}$)</td>
<td>$k_{ex}$ (s$^{-1}$)</td>
<td>$\overline{V}/V_s$</td>
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<td>$1.66 \times 10^7$</td>
<td>0.30</td>
<td>$3.0 \times 10^6$</td>
<td>$5.0 \times 10^{-7}$</td>
<td>$3.3 \times 10^{-6}$</td>
<td>0.30 $- 30$</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
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Supporting References and Notes
