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# COMMENTS

## Comments on “Stirring Effects and Phase-Dependent Inhomogeneity in Chemical Oscillations: The Belousov−Zhabotinsky Reaction in a CSTR”

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The paper of Ali and Menzinger[1] deals with the modeling of the stirring effect in the Belousov−Zhabotinsky (BZ) reaction on the basis of the flow-Oregonator by the cellular mixing (CM) model. Each cell of the model is a homogeneous batch reactor where the Oregonator is solved by ordinary differential equations (ODEs). Flow conditions and external fluctuations are simulated by replacing a pair of randomly chosen cells at time interval $\tau_f$ with two new cells with feedstream concentrations.

As the main result of the study, the authors present the dependence of the probability distribution function (pdf) $P$ on the phase of the oscillation period $T$ as well as the connection between $P$ and the stirring effect (the dependence of oscillation amplitude and period on stirring rate) in a CSTR. The authors believe that external noise dominates in the CSTR, and therefore they use the CM model which accounts only for the contribution of extrinsic noise to the pdf. However, it is not easy to determine only by theoretical means without experimental examination, whether internal fluctuations or external noise dominates in the stirring effect, because different theoretical models lead to different results. If such experiments are lacking, or if they show that inner fluctuations are important to some extent for the comprehension of the stirring effects, they should not be neglected in theoretical models.

To illustrate the importance of inner fluctuations, which are present both in a batch reactor and in CSTR, I applied in this work the method of probability cellular automaton (PCA)[2,3] (which accounts for inner fluctuations automatically) to the stochastic batch-Oregonator and flow-Oregonator *with Ali and Menzinger’s set of constants*. The results are presented in Table 1. For the case of flow-Oregonator, the calculations were made only for $k_1h^2 = 2$ M$^{-1}$ s$^{-1}$, and corresponding results are given in Table 1 in parentheses.

**TABLE 1: Values of the Oscillation Period $T$ and Ratio of the Dispersion $\sigma_z$ to the Average Value $\langle z\rangle$ at Various $k_1$ and Characteristic Mixing Time $\tau_{mix}$ in the Stochastic Oregonator[a]**

| $k_1h^2$/ (M$^{-1}$ s$^{-1}$) | $\tau_{mix}$/s | $T$/s | $T_{max}/T$ | $(\sigma_z/\langle z\rangle)_{ev-T}$ | $(\sigma_z/\langle z\rangle)_{max}$ |
|---|---|---|---|---|---|
| 5 | 0.0012 | 0.363 ± 0.003 | 1 | 1.022 | 1.14 |
| 5 | 0.0091 | 0.355 ± 0.005 | 1.02 | 1.88 | 3 |
| 5 | 0.1250 | 0.356 ± 0.01 | 1.02 | 7.05 | 11.0 |
| 2 | 0.00026 | 0.654 ± 0.005 | 1 | 1.003 | 1.12 |
| 2 | 0.00026 | (0.673 ± 0.005) | (1) | (1.0034) | (1.142) |
| 2 | 0.0012 | 0.623 ± 0.006 | 1.05 | 1.05 | 1.17 |
| 2 | 0.0012 | (0.645 ± 0.008) | (1.043) | (1.045) | (1.18) |
| 2 | 0.0091 | 0.56 ± 0.004 | 1.17 | 2.32 | 3.52 |
| 2 | 0.0091 | (0.571 ± 0.02) | (1.18) | (2.34) | (3.67) |
| 2 | 0.1250 | 0.51 ± 0.007 | 1.28 | 9.75 | 17.45 |
| 2 | 0.1250 | (0.53 ± 0.02) | (1.27) | (15.3) | (23.3) |
| 0.5 | 0.0012 | 1.92 ± 0.01 | 1 | 1.07 | 1.27 |
| 0.5 | 0.0091 | 1.23 ± 0.01 | 1.56 | 2.76 | 4.9 |
| 0.5 | 0.0330 | 0.88 ± 0.03 | 2.18 | 16 | 26.2 |
| 0.5 | 0.1250 | chaos | | | |

[a] $\sigma_z$ is the dispersion of $z_i$, where $z_i$ is a number of $Z$ particles in the $i$th cell of the PCA; $(\sigma_z/\langle z\rangle)_{ev-T}$ is the ratio of the dispersion $\sigma_z$ to $\langle z\rangle$ averaged over the oscillation period $T$, where $\langle z\rangle$ is determined by averaging $z_i$ all over the cells of the PCA; the maximum ratio $(\sigma_z/\langle z\rangle)_{max}$ is achieved at the fast phase of oscillations; $T_{max}$ is the value of the period $T$ when $\tau_{mix} \ll (ak_3h)^{-1}$; the number $N_0$ of automaton cells equals 32 × 32 (for the case of $k_1h^2 = 2$ M$^{-1}$ s$^{-1}$ the Oregonator model was simulated also at $N_0 = 64 \times 64$ and the oscillation period remained constant); the volume $V_m$ assigned to a single automaton cell was chosen to equal $V_m = 3 \times 10^7$ M$^{-1}$/$N_A$, where $N_A$ is the Avogadro number (period $T$ depends on $V_m$, but the character of the dependence of $T$ on $\tau_{mix}$ does not change at different $V_m$; the larger the $V_m$, the closer the values of $T$ obtained by the PCA method at small $\tau_{mix}$ to the value of $T$ obtained from the solution of corresponding ODEs). Oregonator constants: $k_1 = 2$ M$^{-3}$ s$^{-1}$, $k_2 = 2 \times 10^8$ M$^{-2}$ s$^{-1}$, $k_3 = 2 \times 10^3$ M$^{-2}$ s$^{-1}$, $k_4 = 4 \times 10^8$ M$^{-1}$ s$^{-1}$, $k_5 = 1$ M$^{-1}$ s$^{-1}$, $a \equiv [BrO_3^-] = 0.3$ M, $h \equiv [H^+] = 1$ M, and $b \equiv [MA] = 20.0$ M. Feedstream numbers of $X$, $Y$, and $Z$ molecules in the case of the CSTR: $x_0 = 0$, $y_0 = z_0 = 150$, (i.e., $[Y]_0 = [Z]_0 = 0.5 \times 10^{-5}$ M), $k_0 = 0.2$ s$^{-1}$.

Several important conclusions can be made from the data of Table 1. First, the stirring effect proved to be explained on the basis of inner fluctuations only. The value of stirring effect at $k_1h^2 = 2$ M$^{-1}$ s$^{-1}$, $T_{max}/T = 1.28$ (at $\tau_{mix} \cong 0.1$ s), does not differ notably from the analogous value obtained by Ali and Menzinger (1.34).[1] An additional consideration of external noise (the case of the CSTR) has practically no effect on the period $T$, dispersion $\sigma_z$, and stirring effect. It is probably the result of using too small volume $V_m$ of a PCA cell and, as a consequence, of a large amplitude of inner fluctuations. A separate study is needed to answer the question about how and to what extent the external noise modifies the value of the stirring effect caused by inner fluctuations.

Second, from the data of Table 1, it follows that the value of the stirring effect grows with a $k_1$ decrease. At $k_1h^2 = 5$ M$^{-1}$ s$^{-1}$, the stirring effect is lacking, but at $k_1h^2 = 0.5$ M$^{-1}$ s$^{-1}$, $T_{max}/T = 2.18$ (at $\tau_{mix} = 0.033$ s). We showed earlier[2,4] that the stirring effect results from the behavior of the Oregonator model during the slow phase and emerges only when the rate of the system’s approach to the critical concentration of the inhibitor $[Y]_{cr} = ak_3/k_2$, Y = Br$^-$, during the slow phase is much smaller than the rate of autocatalysis (the fast phase), i.e., when inequality 1 holds.

$$k_1h/k_3 < 0.01 \tag{1}$$

while in the opposite case the stirring effect is hardly noticeable. Inequality 1 is fulfilled in the article of Ali and Menzinger.[1] In

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this connection it would be interesting to check how the stirring effect varies in the CM model at different $k_1$.

And, at last, from the data of Table 1 it follows that the dispersion grows with an increase in $\tau_{\mathrm{mix}}$ at all $k_1$, but the period $T$ remains practically constant at $k_1h^2 = 5$ M$^{-1}$ s$^{-1}$. Hence, the variation in pdf $P$ does not always lead to the changes in such observed values as the oscillation period and amplitude.

## References and Notes

(1) Ali, F.; Menzinger, M. *J. Phys. Chem. A* **1997**, *101*, 2304−2309.

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