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

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In his Comment[1] to our paper,[2] Vanag revives the once current view[4] that the system inhomogeneities that give rise to stirring effects in nonlinear reactions are due to internal, statistical fluctuations in particle density, rather than to other extrinsic sources of inhomogeneous noise, and he bases his claims on results of a calculation using a probabilistic cellular automaton model.[3]

All cellular mixing[2] models are mesoscopic and unsuited to deal realistically with the concentration fluctuations that occur on a molecular scale and that are the sources of nucleative dynamics. By treating a mesoscopic cell rather than molecules as the elementary, fluctuating entity, one jumps over many orders of magnitude in particle number $N$ and in the relative amplitude $A = N^{-1/2}$ of fluctuations.

Let us look at a specific example: consider first a reactive fluid with concentrations of the order of 1 mM $\approx 6.7 \times 10^{17}$ molecules/cm$^3$. And consider also a 2-D mesoscopic cell model with $N^2 = 100 \times 100 = 10^4$ cells of a size that is of the order of the Kolmogorov length $L_K \approx 10\ \mu$m. It describes a subvolume with side length $100 \times 10\ \mu\text{m} = 1$ mm, where a reference area (volume) of 1 cm$^2$ contains $10^6$ cells/cm$^2$. In 1 cm$^3$ of the molecular fluid the relative fluctuation amplitude is $A_{\text{molec}} = 1.2 \times 10^{-9}$; in 1 cm$^2$ of the 2-D cellular fluid it is $A_{\text{cell}} = 10^{-3}$. Hence, the cellular model predicts fluctuations that are $1.2 \times 10^6$ times bigger than those on the molecular level. In view of this it is understandable why Vanag's CA model weighs statistical fluctuations so heavily. In a CSTR it even predicts that they dominate over the inflow-induced inhomogeneities.

The "real", molecular fluctuation amplitude $A_{\text{molec}}$ is probably too small[4] to outweigh other likely sources of system inhomogeneity. The best understood case is that of the CSTR,[5] for which we have now quantitative evidence[6] supported by simulations and experiments[6,7] that confirms the earlier view[8] that the primary inhomogeneity, responsible for stirring effects in bistable systems, arises from the forcing of the CSTR by the inflow stream. For systems with one dynamical variable, the intensity $\sigma^2$ of the reactor inhomogeneity, which is related to the observed fluctuation intensity, scales as[6,7b]

$$\sigma^2 \approx t_{\text{mix}}/t_{\text{flow}}(x - x_0)^2$$

i.e., linearly with mixing time $t_{\text{mix}} \approx S^{-1}$ (where $S$ = stirring rate) and with $(x - x_0)^2$, the square difference between the values of the dynamical variable in the reactor and in the inflow. The stirring effect, i.e., the shift $\Delta$ of the stochastic steady state $x_s$ from its deterministic, high-stirring limit $x_d$, scales linearly with the intensity of the inhomogeneity[6,7]

$$\Delta \approx \sigma^2$$

This demonstrates the essential connection of the shift $\Delta$ with the fluctuations on the stochastic level and quantitatively confirms the earlier view[8] on the origin of the inhomogeneities. Physically similar scaling connections may be expected from extending these results on bistability to oscillating systems—the subject of Vanag's Comment.

In batch reactors, less may be said that is of general validity, except that concentration fluctuations whose relative amplitude exceeds the above estimate for statistical fluctuations of $A_{\text{molec}} = 1.2 \times 10^{-9}$ and whose spatial coherence length exceeds the Kolmogorov length $L_K$ are a priori candidates for a stirring effect. Indeed, a rapidly reacting mixture that is homogeneous to less than this value may be difficult to prepare: reaction gives rise to reaction−diffusion and to phase waves, and, if the reaction is significantly exo- or endothermic, to temperature gradients that feed back onto the reaction rate. Different concrete scenarios have been proposed to explain stirring effects in batch reactors, including gas exchange with the surroundings, reaction catalyzed at an interface, adsorption at an interface, and the acceleration of diffusion-limited reactions by turbulence. Vanag's kinetic criterion (eq 1) for a large stirring effect in the Oregonator is interesting and invites further numerical and experimental validation.

In view of the above estimate, it may be difficult to prepare an initially homogeneous system and to unambiguously establish a purely nucleation-induced stirring effect. In conclusion, we believe that the cellular automaton model[3] does not realistically describe the concentration fluctuations in the medium for reasons given above and that at least for the CSTR it may be considered as well established that the reactor inhomogeneities that are the source of stirring effects arise from external forcing by the inflow.

## References and Notes

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