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Spontaneous Appearance of Chirally Asymmetric Steady States in an Oregonator-Based Reaction Model

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A chiral symmetry-breaking reaction model was constructed based on the Oregonator model, which was proposed to explain the oscillatory behavior of the Belousov–Zhabotinskii reaction by Field, Körös, and Noyes. Its symmetry-breaking transition results in the dominance of one enantiomer, and the disappearance of the other. Depending on the parameter values, an asymmetric steady state, symmetric steady state, or oscillatory behavior with either the same or different amplitudes is exhibited. Numerous chemical oscillation systems have been previously reported, and these systems always include autocatalytic processes. Accordingly, if the autocatalyst in these experimental systems has optical isomers and each isomer catalyzes its own production, the spontaneous appearance of a chiral symmetry-breaking state is expected in the chemical oscillation system under the appropriate experimental conditions.

An intrinsic characteristic of living organisms is the presence of optically active and enantiomerically pure molecules.[1–6] To date, several studies have attempted to account for the origin of chiral molecules in nature, however, its true origin remains unknown. Both biotic and abiotic theories for the origin of homochirality have been proposed.[4] Biotic theories suggest that primitive life emerged in a racemic environment, and subsequent evolution of this life has gradually selected one enantiomer. In contrast, abiotic theories suggest that an enantiomeric excess of one isomer was present before primitive life. In short, the formation and evolution of primitive biomolecules (DNA, RNA, peptides, and biological chemicals) would have been impossible without the establishment of an enantiomeric imbalance.[6,7] Abiotic theories suggest that a small initial inhomogeneity may have occurred either by chance[8,9] or in a determinate way,[10] and that the inhomogeneity could be amplified by means of an autocatalytic process.[8–16] Abiotic theories are currently widely accepted, even though no explicit experimental evidence has been found.

A number of reaction models[8–16] that explain chiral separation have been discussed in the context of dissipative structures far from equilibrium.[17] Frank[8] devised a simple reaction model with stereoselective autocatalysis and mutual inhibition, and showed spontaneous appearance of an optically active state under symmetric conditions. Kondepudi and Nelson modified Frank's reaction scheme and have investigated chiral symmetry-breaking transitions.[13]

On the other hand, Soai and co-workers have reported interesting experiments on chiral amplification of a small initial enantiomeric excess.[18–20] In a recent article, they reported a case in which one of the enantiomers was produced from achiral reactants in the absence of chiral sources.[21] This is thought to be the first article reporting an absolute asymmetric synthesis in the laboratory.

Previously, we reported some hypothetical reaction models[15,16] that can generate and maintain a chiral asymmetric steady state under far-from-equilibrium conditions. These investigations suggested that the reaction model of every chemical oscillation system could be easily rewritten into a reaction model with chiral symmetry-breaking states. Thus, if the reaction intermediates of a chemical oscillation system are chiral and possess enantiomers, the spontaneous appearance of a chiral asymmetric state is expected.

The Belousov–Zhabotinskii (BZ) reaction[22] is the most widely investigated chemical oscillation system. The reaction has been thoroughly investigated by Field, Körös, and Noyes.[23] Furthermore, the kinetic mechanism giving rise to the oscillation is now believed to be well-established. In these investigations, eleven reactions were studied in order to account for the qualitative and quantitative observations in the BZ reaction.[23,24] The reaction mechanism is referred to as the FKN mechanism. A simplified three-variable Oregonator[25] has been constructed for this mechanism. This simplified mechanism has been used for investigations of chemical instabilities and oscillations. Tyson transformed the rate equations for the Oregonator model to the dimensionless form.[24] Herein, we modify the Oregonator scheme to a reaction model for chiral symmetry-breaking behavior.

Oregonator Model

The Oregonator model for the B–Z reaction in open systems is given by the following equations:[26]

$$\mathrm{A} + \mathrm{Y} \xrightarrow{k_1} \mathrm{X} + \mathrm{P}, \tag{1}$$

$$\mathrm{A} + \mathrm{X} \xrightarrow{k_2} 2\mathrm{X} + 2\mathrm{Z}, \tag{2}$$

$$\mathrm{X} + \mathrm{Y} \xrightarrow{k_3} 2\mathrm{P}, \tag{3}$$

$$2\mathrm{X} \xrightarrow{k_4} \mathrm{A} + \mathrm{P}, \tag{4}$$

$$\mathrm{B} + \mathrm{Z} \xrightarrow{k_5} \left(\frac{f}{2}\right)\mathrm{Y}, \tag{5}$$

where the concentrations of A and B are assumed to be constant. As the oregonator is a reduced simple model from the complicated FKN mechanism, the parameter f involves various types of approximation in the reduction.[26] The concentrations of the respective chemical species are denoted in italics, thus giving the following rate equations for the concentrations of X, Y, and Z, respectively:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_1AY + k_2AX - k_3XY - 2k_4X^2, \tag{6}$$

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = -k_1AY - k_3XY + \frac{f}{2}k_5BZ, \tag{7}$$

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = 2k_2AX - k_5BZ. \tag{8}$$

Here, according to Tyson's method,[25] where

$$x = X/X_0,\ y = Y/Y_0,\ z = Z/Z_0 \quad \text{and} \quad \tau = t/T_0. \tag{9}$$

Eqs. 6–8 can be rewritten into the following dimensionless rate equations:

$$\varepsilon\frac{\mathrm{d}x}{\mathrm{d}\tau} = qy - xy + x(1 - x), \tag{10}$$

$$\sigma\frac{\mathrm{d}y}{\mathrm{d}\tau} = -qy - xy + fz, \tag{11}$$

$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = x - z, \tag{12}$$

where

$$\begin{aligned} &X_0 = k_2A/2k_4,\ Y_0 = k_2A/k_3,\ Z_0 = (k_2A)^2/k_4k_5B,\\ &T_0 = 1/k_5B,\ \varepsilon = k_5B/k_2A,\\ &\sigma = 2k_4k_5B/k_2k_3A \quad \text{and} \quad q = 2k_1k_4/k_2k_3. \end{aligned} \tag{13}$$

If $k_1 = 1.28$, $k_2 = 8.0$, $k_3 = 8.0 \times 10^5$, $k_4 = 2.0 \times 10^3$, $k_5 = 1.0$, $A = 0.06$, and $B = 0.02$, the parameters ε, σ, and q are then[26]

$$\varepsilon = 4 \times 10^{-2},\ \sigma = 2 \times 10^{-4}, \quad \text{and} \quad q = 8 \times 10^{-4}. \tag{14}$$

Substitution of $\mathrm{d}x/\mathrm{d}\tau = \mathrm{d}y/\mathrm{d}\tau = \mathrm{d}z/\mathrm{d}\tau = 0$, and $x \neq 0$ into Eqs. 10–12 gives

$$x^2 + (f + q - 1)x - (1 + f)q = 0 \tag{15}$$

for the real steady state of the Oregonator model. The positive solution of this equation is denoted by x_s, in which the subscript s denotes steady state (or symmetric steady state) hereafter. Then,

$$y_\mathrm{s} = \frac{fx_\mathrm{s}}{q + x_\mathrm{s}} \tag{16}$$

and

$$z_\mathrm{s} = x_\mathrm{s}. \tag{17}$$

According to the ordinary linearized stability analysis,[17] the steady state is unstable when $0.523 \leq f \leq 2.309$, over which oscillatory behavior occurs.

Symmetry-Breaking Transition

Here, let X and Y be chiral compounds. That is, X can be defined by its enantiomers X_L and X_D, and Y by its enantiomers, Y_L and Y_D. Then, reaction model 1–5 can be rewritten as

$$\mathrm{A} + \mathrm{Y_L} \xrightarrow{k_1} \mathrm{X_L} + \mathrm{P}, \qquad \mathrm{A} + \mathrm{Y_D} \xrightarrow{k_1} \mathrm{X_D} + \mathrm{P}, \tag{18}$$

$$\mathrm{A} + \mathrm{X_L} \xrightarrow{k_2} 2\mathrm{X_L} + 2\mathrm{Z}, \qquad \mathrm{A} + \mathrm{X_D} \xrightarrow{k_2} 2\mathrm{X_D} + 2\mathrm{Z}, \tag{19}$$

$$\mathrm{X_L} + \mathrm{Y_L} \xrightarrow{k_3} 2\mathrm{P}, \qquad \mathrm{X_D} + \mathrm{Y_D} \xrightarrow{k_3} 2\mathrm{P}, \tag{20}$$

$$2\mathrm{X_L} \xrightarrow{k_4} \mathrm{A} + \mathrm{P}, \qquad 2\mathrm{X_D} \xrightarrow{k_4} \mathrm{A} + \mathrm{P}, \tag{21}$$

$$\mathrm{B} + \mathrm{Z} \xrightarrow{k_5} \left(\frac{f}{2}\right)\mathrm{Y_L}, \qquad \mathrm{B} + \mathrm{Z} \xrightarrow{k_5} \left(\frac{f}{2}\right)\mathrm{Y_D}. \tag{22}$$

And the rate equations have the following forms

$$\frac{\mathrm{d}X_\mathrm{L}}{\mathrm{d}t} = k_1AY_\mathrm{L} + k_2AX_\mathrm{L} - k_3X_\mathrm{L}Y_\mathrm{L} - 2k_4{X_\mathrm{L}}^2, \tag{23}$$

$$\frac{\mathrm{d}X_\mathrm{D}}{\mathrm{d}t} = k_1AY_\mathrm{D} + k_2AX_\mathrm{D} - k_3X_\mathrm{D}Y_\mathrm{D} - 2k_4{X_\mathrm{D}}^2, \tag{24}$$

$$\frac{\mathrm{d}Y_\mathrm{L}}{\mathrm{d}t} = -k_1AY_\mathrm{L} - k_3X_\mathrm{L}Y_\mathrm{L} + \frac{f}{2}k_5BZ, \tag{25}$$

$$\frac{\mathrm{d}Y_\mathrm{D}}{\mathrm{d}t} = -k_1AY_\mathrm{D} - k_3X_\mathrm{D}Y_\mathrm{D} + \frac{f}{2}k_5BZ, \tag{26}$$

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = 2k_2A(X_\mathrm{L} + X_\mathrm{D}) - 2k_5BZ. \tag{27}$$

The dimensionless rate equations are[24]

$$\varepsilon\frac{\mathrm{d}x_\mathrm{L}}{\mathrm{d}\tau} = qy_\mathrm{L} - x_\mathrm{L}y_\mathrm{L} + x_\mathrm{L}(1 - x_\mathrm{L}), \tag{28}$$

$$\varepsilon\frac{\mathrm{d}x_\mathrm{D}}{\mathrm{d}\tau} = qy_\mathrm{D} - x_\mathrm{D}y_\mathrm{D} + x_\mathrm{D}(1 - x_\mathrm{D}), \tag{29}$$

$$\sigma\frac{\mathrm{d}y_\mathrm{L}}{\mathrm{d}\tau} = -qy_\mathrm{L} - x_\mathrm{L}y_\mathrm{L} + fz, \tag{30}$$

$$\sigma\frac{\mathrm{d}y_\mathrm{D}}{\mathrm{d}\tau} = -qy_\mathrm{D} - x_\mathrm{D}y_\mathrm{D} + fz, \tag{31}$$

$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = x_\mathrm{L} + x_\mathrm{D} - 2z, \tag{32}$$

where

$$\begin{aligned} &x_\mathrm{L} = X_\mathrm{L}/X_0,\ x_\mathrm{D} = X_\mathrm{D}/X_0,\ y_\mathrm{L} = Y_\mathrm{L}/Y_0,\ y_\mathrm{D} = Y_\mathrm{D}/Y_0,\\ &z = Z/Z_0,\ \tau = t/T_0,\ X_0 = k_2A/2k_4,\ Y_0 = k_2A/k_3,\\ &Z_0 = (k_2A)^2/k_4k_5B,\ T_0 = 1/k_5B,\ \varepsilon = k_5B/k_2A,\\ &\sigma = 2k_4k_5B/k_2k_3A, \quad \text{and} \quad q = 2k_1k_4/k_2k_3. \end{aligned} \tag{33}$$

In the following calculations, the same values as those used for Eq. 14 were used.

As $\mathrm{d}x_\mathrm{L}/\mathrm{d}\tau = \mathrm{d}x_\mathrm{D}/\mathrm{d}\tau = \mathrm{d}y_\mathrm{L}/\mathrm{d}\tau = \mathrm{d}y_\mathrm{D}/\mathrm{d}\tau = \mathrm{d}z/\mathrm{d}\tau = 0$ at the steady states, we get

$$qy_\mathrm{L} - x_\mathrm{L}y_\mathrm{L} + x_\mathrm{L}(1 - x_\mathrm{L}) = 0, \tag{34}$$

$$qy_\mathrm{D} - x_\mathrm{D}y_\mathrm{D} + x_\mathrm{D}(1 - x_\mathrm{D}) = 0, \tag{35}$$

$$-qy_\mathrm{L} - x_\mathrm{L}y_\mathrm{L} + fz = 0, \tag{36}$$

$$-qy_\mathrm{D} - x_\mathrm{D}y_\mathrm{D} + fz = 0, \tag{37}$$

$$x_\mathrm{L} + x_\mathrm{D} - 2z = 0. \tag{38}$$

In order to obtain the asymmetric solution ($x_\mathrm{L} \neq x_\mathrm{D}$) to Eqs. 34–38, $\alpha = x_\mathrm{L} + x_\mathrm{D}$ and $\beta = x_\mathrm{L}x_\mathrm{D}$ were substituted into Eqs. 34–38, and the following equations were derived.

$$\begin{aligned} &2\alpha^3 + (4q + f - 4)\alpha^2 + (2 + 2q^2 + 2fq - 6q - f)\alpha\\ &\quad + 2q(1 - q) = 0, \end{aligned} \tag{39}$$

$$\beta = \frac{q}{1 - \alpha}[\alpha^2 + (q + f - 1)\alpha - q]. \tag{40}$$

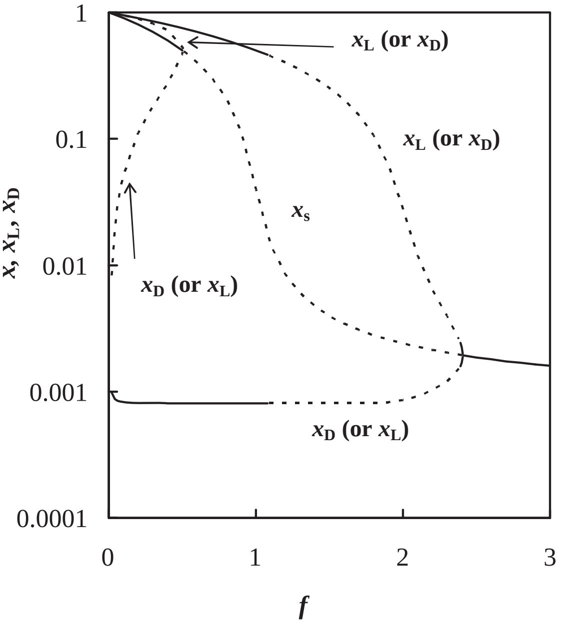

Fig. 1. Symmetric and asymmetric steady-state loci of the chiral symmetry-breaking chemical system. The locus x_s represents the symmetric steady state, which is calculated from Eq. 15, where $\varepsilon = 4 \times 10^{-2}$, $\sigma = 2 \times 10^{-4}$, and $q = 8 \times 10^{-4}$.

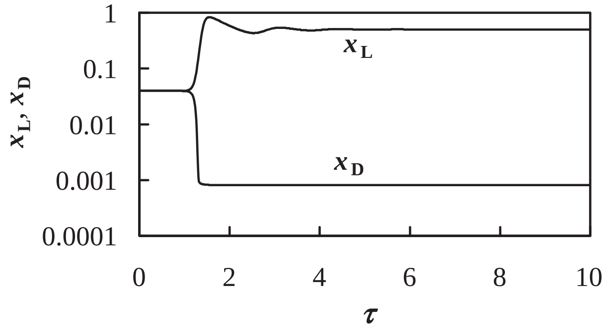

Fig. 2. Time evolution of x_L and x_D starting from a vicinity of the symmetric steady state ($x_L = x_s + 10^{-12}$, $x_D = x_s$, $y_L = y_s$, $y_D = y_s$, $z = z_s$). x_s, y_s, and z_s are calculated from Eqs. 15–17. $f = 1.0$, $\varepsilon = 4 \times 10^{-2}$, $\sigma = 2 \times 10^{-4}$, and $q = 8 \times 10^{-4}$.

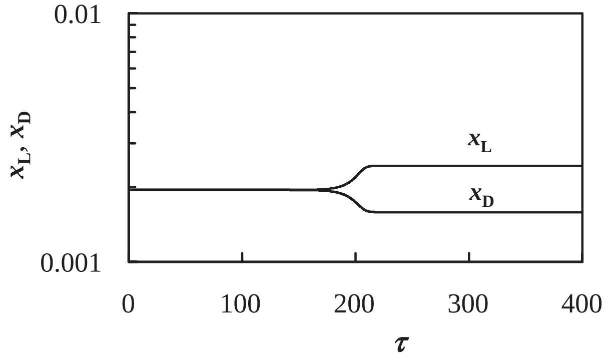

Fig. 3. Time evolution of x_L and x_D starting from the vicinity of the symmetric steady state ($x_L = x_s + 10^{-12}$, $x_D = x_s$, $y_L = y_s$, $y_D = y_s$, $z = z_s$). x_s, y_s, and z_s are calculated from Eqs. 15–17. $f = 2.39$, $\varepsilon = 4 \times 10^{-2}$, $\sigma = 2 \times 10^{-4}$, and $q = 8 \times 10^{-4}$.

In the range $0 \leq f < 3$, Eqs. 39 and 40 give two positive solutions α_1 and α_2 ($\alpha_1 > \alpha_2$), and the corresponding values for β_1 and β_2. These give x_L and x_D, which are plotted in Fig. 1. When $0 \leq f < 0.502$, α_1 and β_1 give positive real values for x_L and x_D, and imaginary values in the range $f \geq 0.502$. On the other hand, α_2 and β_2 give positive real values for x_L and x_D in the range $0 < f \leq 2.406$, beyond which x_L and x_D become imaginary. These are compiled in Fig. 1.

The symmetric steady states for the reaction model 18–22 are also determined by setting $x_L = x_D$ and $y_L = y_D$ in Eqs. 34–38, giving the same equations as shown in 15–17. The symmetric steady states are also shown in Fig. 1. The local stability of each steady state was determined according to the ordinary linearized stability analysis.[17] The stable and unstable steady states are shown by solid and dotted lines respectively. The symmetric steady states are unstable in the range $0.502 \leq f \leq 2.406$, in which either an asymmetric steady state or oscillatory behavior occurs.

In the range $0 < f \leq 0.501$, there are two asymmetric steady states and one symmetric steady state. As one of the asymmetric steady states is unstable, either a symmetric or asymmetric steady state emerges, depending on the initial state. On the other hand, as the asymmetric steady state only is stable when $0.502 \leq f \leq 1.083$, it appears independently of the initial state. This suggests that the asymmetric steady state appears eventually, even if the initial state is in the vicinity of the symmetric steady state. An example is shown in Fig. 2.

When $1.084 \leq f \leq 2.382$, both the symmetric and asymmetric steady states are unstable and, therefore, the system falls into an oscillatory state. In the range $1.084 \leq f \leq 2.188$, x_L and x_D oscillate simultaneously with the same amplitude and phase, but oscillate with different amplitudes when $2.189 \leq f \leq 2.382$. The change in the oscillation mode occurs suddenly and distinctly at $f = 2.188$.

The asymmetric steady states stabilize again when $2.383 \leq f \leq 2.406$, which occurs independently of the initial state. Figure 3 shows the case in which $f = 2.39$. When $f \geq 2.407$, only the symmetric steady state appears.

The BZ reaction is an oxidation reaction of malonic acid by acid bromate ion, and is catalyzed by a cerium(III) and (IV) couple. Though the mechanism of the BZ reaction is extremely complicated, and includes more than 20 steps,[27] the key reactions giving rise to oscillation are summarized in the Oregonator model, in which the following reagents are essential.

$$X = HBrO_2,\ Y = Br^-,\ Z = Ce^{IV}.$$

As X and Y are achiral chemical reagents, we cannot expect the construction of an experimental chiral symmetry-breaking system from the BZ reaction. However, if an experimental chemical oscillation system whose intermediates are chiral and self-reproducing is identified sometime in the future, then spontaneous appearance of a chirally asymmetric state may be realized in the laboratory. This may be feasible, because chemical oscillation systems are not unusual,[28] and various different systems are expected to be identified in the future.

References

1 S. Mason, *Chem. Soc. Rev.* **1988**, *17*, 347.

2 M. de Min, G. Levy, J. C. Micheau, *J. Chim. Phys.* **1988**, *85*, 603.

3 W. A. Bonner, *Origins Life Evol. Biosphere* **1991**, *21*, 59.

4 W. A. Bonner, in *Physical Origin of Homochirality in Life*, ed. by D. B. Cline, AIP Press, New York **1995**, pp. 17–49.

5 P. Frank, A. Bonner, R. Zare, in *Chemistry for the 21st Century*, ed. by E. Keinan, I. Schechter, Wiley, Weinheim **2001**, pp. 175–208.

6 V. I. Goldanskii, V. V. Kuz'min, *Z. Phys. Chem.* **1988**, *269*, 216.

7 G. F. Joyce, G. M. Visser, C. A. A. van Boeckel, J. H. van Boom, L. E. Orgel, J. van Westrenen, *Nature* **1984**, *310*, 602.

8 F. C. Frank, *Biochim. Biophys. Acta* **1953**, *11*, 459.

9 K. Iwamoto, M. Seno, *J. Chem. Phys.* **1979**, *70*, 5858.

10 D. K. Kondepudi, G. W. Nelson, *Nature* **1985**, *314*, 438.

11 F. F. Seelig, *J. Theor. Biol.* **1971**, *31*, 355.

12 K. Iwamoto, M. Seno, *J. Chem. Phys.* **1982**, *76*, 2347.

13 D. K. Kondepudi, G. W. Nelson, *Phys. Lett.* **1983**, *50*, 1023.

14 D. K. Kondepudi, G. W. Nelson, *Physica A* **1984**, *125*, 465.

15 K. Iwamoto, *Phys. Chem. Chem. Phys.* **2002**, *4*, 3975.

16 K. Iwamoto, *Phys. Chem. Chem. Phys.* **2003**, *5*, 3616.

17 P. Glansdorff, I. Prigogine, *Thermodynamic Theory of Structure, Stability, and Fluctuations*, Wiley, London **1971**, Chap. 14.

18 K. Soai, T. Shibata, H. Morioka, K. Choji, *Nature* **1995**, *378*, 767.

19 T. Shibata, J. Yamamoto, N. Matsumoto, S. Yonekubo, S. Osanai, K. Soai, *J. Am. Chem. Soc.* **1998**, *120*, 12157.

20 K. Soai, I. Sato, *Chirality* **2002**, *14*, 548.

21 K. Soai, I. Sato, T. Shibata, S. Komiya, M. Hayashi, Y. Matsueda, H. Imamura, T. Hayase, H. Morioka, H. Tabira, J. Yamamoto, Y. Kowata, *Tetrahedron: Asymmetry* **2003**, *14*, 185.

22 A. M. Zhabotinskii, *Biophysika* **1964**, *9*, 306.

23 R. J. Field, E. Körös, R. M. Noyes, *J. Am. Chem. Soc.* **1972**, *94*, 8649.

24 J. J. Tyson, *J. Phys. Chem.* **1982**, *86*, 3006.

25 R. J. Field, R. M. Noyes, *J. Chem. Phys.* **1974**, *60*, 1877.

26 P. Gray, S. K. Scott, *Chemical Oscillations and Instabilities*, Clarendon Press, Oxford **1990**, Chap. 14.

27 D. Edelson, R. J. Field, R. M. Noyes, *Int. J. Chem. Kinet.* **1975**, *7*, 417.

28 O. Gurel, D. Gurel, *Oscillations in Chemical Reactions*, Springer-Verlag, New York **1983**.