Synergetic Mechanisms of Chiral Symmetry Breaking in Prebiotic Evolution

P. BABINEC[1] and J. KREMPASKÝ[2]

1 *Department of Biophysics and Chemical Physics, Faculty of Mathematics and Physics, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia*
2 *Department of Physics, Faculty of Electrical Engineering, Slovak Technical University, Ilkovičova 3, 812 19 Bratislava, Slovakia*

Abstract. It was shown on the Frank autocatalytic reaction-diffusion scheme that strong environmental fluctuations, conditioned by external noise (e.g. sunlight fluctuation) and external macroscopic flows (e.g. ebb and flow), typical for conditions on prebiotic earth, may have been beneficial for chiral symmetry breaking and formation and stabilization of biomolecular homochirality.

Key words: Synergetics — Evolution — Chirality — Fluctuations — Symmetry Breaking

Introduction

As it has been shown experimentally, life based on self-replication of organic homochiral polymers could have originated only if the prebiotic organic medium was capable of spontaneous symmetry breaking to the chirally pure state (Joyce et al. 1984; Goldanskii et al. 1986; Lacey et al. 1993).

The first model of spontaneous mirror-symmetry breaking of racemic mixture was proposed by Frank (1953). This idea was later generalized and investigated in detail theoretically (Morozov 1978; Kondepudi and Nelson 1985) and experimentally (Tjivikuma et al. 1990; Kondepudi et al. 1993). Also other autocatalytic processes of enantiomer formations have been proposed (Aleksandrov 1990; Mikhailov and Loskutov 1991).

Spontaneous chiral symmetry breaking can occur not only in nonequilibrium chemical systems, but also due to the Bose-Einstein condensation conditioned by

Correspondence to: P. Babinec, Department of Biophysics and Chemical Physics, Faculty of Mathematics and Physics, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia

mixing of electromagnetic and weak interactions (Salam 1991) and long-range interactions of chiral biomolecules (Babincová and Babinec 1994).

It is clear that the process of synthesis of enantiomers occurs in a fluctuating environment. On a model chemical system it has been recently shown (Krempaský and Krejčíová 1993) that even in the absence of a deterministic bifurcation point, spontaneous pure noise-induced transition exists which may produce chirally pure medium.

Different possible mechanisms of chiral symmetry breaking may occur also in reaction-diffusion systems. As it is known reaction dynamics in such systems in the presence of diffusion and macroscopic flows (wind, ebb and flow, etc.) may lead to various spatio-temporal structures where the concentrations of components are complicated functions of space and time coordinates.

The aim of this paper was to investigate the influence of external noise, diffusion and macroscopic flows on a nonequilibrium chemical system based on generalized Frank kinetic scheme of autocatalytic reactions.

Evolution equations

Let us consider the following scheme of chemical reactions which represents a generalized Frank scheme of autocatalytic enantiomer formations (Frank 1953; Kondepudi and Nelson 1983, 1985; Tjivikuma et al. 1990; Kondepudi et al. 1993; Goldanskii and Kuzmin 1988)

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1^{\mathrm{L}}} \mathrm{L}; \qquad \mathrm{A} + \mathrm{B} \xrightarrow{k_1^{\mathrm{D}}} \mathrm{D} \tag{1a}$$

$$\mathrm{A} + \mathrm{B} + \mathrm{L} \underset{k_{-2}^{\mathrm{L}}}{\overset{k_2^{\mathrm{L}}}{\rightleftharpoons}} 2\,\mathrm{L}; \qquad \mathrm{A} + \mathrm{B} + \mathrm{D} \underset{k_{-2}^{\mathrm{D}}}{\overset{k_2^{\mathrm{D}}}{\rightleftharpoons}} 2\,\mathrm{D} \tag{1b}$$

$$\mathrm{L} + \mathrm{D} \xrightarrow{k_3} \mathrm{C} \tag{1c}$$

L, D denote L- and D-optical enantiomers, A, B and C are achiral reagents and $k_i^{\mathrm{L}\ \mathrm{D}}$ are reaction rate constants. Due to the symmetry we put $k_i^{\mathrm{L}} = k_i^{\mathrm{D}} = k_i$. Autocatalytic reaction (1b) is to be thought of rather as an effective reaction that represents a more complicated set of reactions. We assume that the concentrations of A and B are maintained constant by a suitable supply, which together with removal of products (1c) maintains the system far from thermodynamic equilibrium.

The scheme of chemical reactions (1) is described by the following kinetic equations for concentrations X_{L} and X_{D} of enantiomers.

$$\frac{\mathrm{d}X_{\mathrm{L}}}{\mathrm{d}t} = F_{\mathrm{L}}(X_{\mathrm{L}}, X_{\mathrm{D}}) \tag{2a}$$

$$\frac{\mathrm{d}X_{\mathrm{D}}}{\mathrm{d}t} = F_{\mathrm{D}}(X_{\mathrm{L}}, X_{\mathrm{D}}) \tag{2b}$$

where

$$F_L(X_L, X_D) = (X_A X_B)k_1 + (X_A X_B)k_2 X_L - k_{-2}X_L^2 - k_3 X_L X_D$$
$$F_D(X_L, X_D) = (X_A X_B)k_1 + (X_A X_B)k_2 X_D - k_{-2}X_D^2 - k_3 X_L X_D$$

For further analysis it is suitable to introduce chiral polarization of the medium $\eta = (X_L - X_D)/(X_L + X_D)$, which is an order parameter for nonequilibrium system described by the kinetic equation of the type (2) and rescaled (dimensionless) total concentration $\theta = \frac{k_2}{2k_1}(X_L + X_D)$.

Equations (2a,b) then take the form

$$\tau \frac{d\eta}{dt} = -\lambda\eta/\theta + A\theta(\eta - \eta^3) \tag{3a}$$
$$\tau \frac{d\theta}{dt} = \lambda + \lambda\theta - (A + B)\theta^2 + A\,\theta^2\eta^2 \tag{3b}$$

where the governing parameter $\lambda = X_A X_B/[4k_1 k_{-2}^2/k_2^2(k_3 - k_{-2})]$, $A = \frac{1}{2}(k_3/k_{-2} - 1)$, $B = \frac{1}{2}(k_3/k_{-2} + 1)$ and $\tau = k_2(k_3 - k_{-2})/4k_1k_{-2}^2$. Using the Haken slaving principle (Haken 1977, 1989; Avetisov et al. 1987) (θ variable is "slaved" by order parameter η, which means that in equation (3b) we put $d\theta/dt = 0$), we obtain an effective evolution equation for η

$$\frac{d\eta}{dt} = -a\eta^3 + a(\lambda - \lambda_c)\eta \tag{4}$$

where $a = k_1 k_{-2}^2/2k_2k_3$. There exists a critical value $\lambda_c = 1$, so that in the region $\lambda < \lambda_c$ the only stable state of the system is the racemic one ($\eta = 0$). Upon reaching the bifurcation point $\lambda = \lambda_c$ this state loses stability and in the region $\lambda > \lambda_c$ there appear two stable mirror-conjugated stationary states with $\eta \neq 0$.

Symmetry breaking influenced by external noise

Due to the omnipresence of environmental fluctuations, equation (4) represents an idealized deterministic case. To describe the realistic situation, we include in equation (4) for the evolution of chiral polarization η, fluctuation of governing parameter λ (multiplicative noise) and additive noise. We get the following stochastic equation of the Stratonowich type

$$\frac{d\eta}{dt} = -a\eta^3 + a(\lambda - \lambda_c)\eta + \sigma_M \eta F_M(t) + \sigma_A F_A(t) \tag{5}$$

where $F_M(t)$ and $F_A(t)$ are independent Gaussian white noises

$$\langle F_{A,M}(t)F_{A,M}(t')\rangle = \delta(t - t'), \quad \langle F_{A,M}(t)\rangle = 0$$

and σ_M and σ_A are intensities of multiplicative and additive noise, respectively.

Due to the fact that additive noise does not change the character of the bifurcation points (Horsthemke and Lefever 1984), it will be further neglected ($\sigma_A = 0$). It is advantageous to proceed to the Fokker-Planck equation corresponding to the Stratonowich equation (4). It is formulated for probability density p(η, t) which describes the probability to find chiral polarization in the interval $\langle \eta, \eta + d\eta \rangle$.

$$\frac{\partial p(\eta,t)}{\partial t} = -\frac{\partial}{\partial \eta}\left[\{a(\lambda - \lambda_c)\eta - a\eta^3 + \frac{1}{2}\sigma_M^2 \eta\}\, p(\eta,t)\right] + \frac{1}{2}\sigma_M^2 \frac{\partial^2}{\partial \eta^2}\left[\eta^2 p(\eta,t)\right] \tag{6}$$

Stationary probability density $p_s(\eta)$ which characterizes the steady-state behaviour $(\partial p(\eta,t)/\partial t = 0)$ of the system under external white noise is easily obtained by integration of equation (6).

$$p_s(\eta) = N\ \eta^{-1+2(\lambda-\lambda_c)a/\sigma_M^2}\ \exp\left[-\frac{a}{\sigma_M^2}\ \eta^2\right] \tag{7}$$

where N is the normalization constant. The extrema of $p_s(\eta)$ may be found from condition $\left.\frac{dp_s(\eta)}{d\eta}\right|_{\eta=\eta_m} = 0$, which give us the following relation

$$a(\lambda - \lambda_c)\eta_m - a\eta_m^3 - \frac{1}{2}\sigma_M^2\ \eta_m = 0 \tag{8}$$

The extrema of $p_s(\eta)$ are the most appropriate indicator for a transition in the steady-state behaviour of the system and may be identified with the macroscopic steady-states of the system (Horsthemke and Lefever 1984). From equation (8) we get

$$\eta_{m1} = 0\ ;\quad \eta_{m2} = \pm\left((\lambda - \lambda_c) - \sigma_M^2/2a\right)^{1/2} \tag{9}$$

If $\lambda < \lambda_c$ stable is stationary state with $\eta = 0$ (racemic state) At $\lambda = \lambda_c$ the racemic stationary state becomes unstable and foı $\lambda > \lambda_c$ a new stationary probability density appears, racemic state is unstable but still the most probable.

At $\lambda > \lambda_c + \sigma_M^2/2a$ the character of $p_s(\eta)$ changes again. The point $\lambda = \lambda_c + \sigma_M^2/2a$ is therefore a noise-induced transition point, where the most probable state with $\eta \neq 0$ acquires a non-zero value and the probability of racemic state $p_s(0) = 0$.

Symmetry breaking due to the diffusion and external flows

In prebiotic era when probably chiral symmetry was broken, factors like macroscopic flows (due to the wind, storm, ebb and flow, etc.) and of course diffusion played an important role. In order to construct a more realistic model of chirality evolution we must consider spatially extended systems. Concentrations of enantiomers are then functions of the spatial coordinate r and evolution equations must be generalized to the form

$$\frac{\mathrm{d}X_{\mathrm{L}}}{\mathrm{d}t} = F_{\mathrm{L}}(X_{\mathrm{L}}, X_{\mathrm{D}}) - \nabla \cdot \gamma_{\mathrm{L}} \tag{10a}$$

$$\frac{\mathrm{d}X_{\mathrm{D}}}{\mathrm{d}t} = F_{\mathrm{D}}(X_{\mathrm{L}}, X_{\mathrm{D}}) - \nabla \cdot \gamma_{\mathrm{D}} \tag{10b}$$

where $\gamma_{\mathrm{L}} = v_{\mathrm{L}}\ X_{\mathrm{L}} - D_{\mathrm{L}}\ \nabla X_{\mathrm{L}}$ and $\gamma_{\mathrm{D}} = v_{\mathrm{D}}\ X_{\mathrm{D}} - D_{\mathrm{D}}\ \nabla X_{\mathrm{D}}$, and $v_{\mathrm{L}}, v_{\mathrm{D}}$ are macroscopic velocities characterizing external flows, and D_{L}, D_{D} are the diffusion coefficients of L and D enantiomers, respectively, which obey the following relation

$$D_{\mathrm{L}}(X_{\mathrm{L}}, X_{\mathrm{D}}) = D_{\mathrm{D}}(X_{\mathrm{D}}, X_{\mathrm{L}}) \tag{11}$$

due to the stereospecific interactions (Craig and Mellor 1976) between D and L enantiomers ($V_{\mathrm{DD}} = V_{\mathrm{LL}} \neq V_{\mathrm{LD}}$). Diffusion coefficient equals only in the racemic state ($X_{\mathrm{L}} = X_{\mathrm{D}}$).

Evolution equations similar to that given by equation (10) have been recently analyzed in connection with plankton distribution on ocean surface in the presence of ebb and flow, which is a situation very similar to that of enantiomer formation in prebiotic evolution. As it has been shown (Malchow 1993a,b), external flows in connection with diffusion lead to strong symmetry breaking of homogeneous state and these factors may also play an important role in the destabilization of racemic state and the formation of regions of homochirality.

This behaviour also follows from generalization of equation (4) to spatially extended reaction systems with diffusion which has now the form of the Landau-Ginzburg equation (Haken 1983)

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -a\eta^3 + b\eta + c\ \nabla^2\eta \tag{12}$$

where a, b and c are constants, or even to the Kuramoto-Tsuzuki equation (Kuramoto 1984)

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -a'|\eta|^2\eta + b'\eta + c'\ \nabla^2\eta \tag{13}$$

where constants a', b', c' and also chiral polarization $\eta(r,t)$ are in general complexly valued.

These equations have a very rich spectrum of solutions (Akhromeieva et al. 1989) in which again the loss of chiral stability is preferred.

Conclusion

Terrestrial mechanisms of the origin of biomolecular homochirality have recently been considered as intrinsically invalid or highly improbable, due to the chaotic and turbulent environment of prebiotic earth (Bonner 1991a,b).

Environmental noise is usually considered only as a disorganizing factor, which favours racemic state. As we have shown, external noise coupled to the order parameter η may induce and stabilize macroscopic state with non-zero chiral polarization.

The source of external noise may be incidental sunlight energy (especially in the ultraviolet range) under which organic substances are formed (Calvin 1969). The opaque particles on fluctuating ocean surface, where the prebiotic evolution probably took place, may generate the desired light noise. The influence of light intensity fluctuations has already been experimentally studied on Briggs-Rauscher reaction, where a noise-induced transition point has been found (De Kepper and Horsthemke 1978).

Also the seemingly racemizing factors like various external flows and diffusion induce a state with broken chiral symmetry, which may be of particular importance in the beginning of prebiotic evolution.

As we have shown on this nonlinear nonequilibrium autocatalytic system influenced by environmental fluctuations, various synergetic mechanisms may lead to self-organization of biomolecular homochirality.

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