SPONTANEOUS BREAKING OF L—D SYMMETRY IN BIOCHEMICAL EVOLUTION

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Abstract: A simple mathematical model is constructed to show that a minute difference $\Delta E$ in the activation energies of L and D isomers of biomolecules is sufficient to achieve optical stereoselection in biochemical evolution. Rate equations describing the competition between self-replicating molecules of two types are shown to exhibit spontaneous breaking of right-left symmetry.

1. Introduction

The richness and diversity of the universe depends on lack of perfect symmetry. The most symmetric universe would be a time reversible homogeneous gravitating system of photons. 'Physics' would become meaningless in such a situation as intelligent beings cannot evolve in this world where there is no 'Chemistry'. In fact if matter is CP invariant a homogeneous photon universe is probably the only possible realization.

The major macroscopic asymmetries in the universe are (1) the arrow of time, ie, the general irreversibility of all natural processes, (2) the inhomogeneity of space, ie, the matter in the universe are lumped into galaxies placed far apart, (3) the chemical asymmetry, ie, nearly symmetric forms of matter allowed by microscopic laws of nature do not exist with equal abundance, either locally or globally.

Although, the macroscopic world is largely asymmetric, the fundamental interactions among elementary particles respect it to a much higher degree of accuracy, parity and time reversal invariance are only slightly violated. Recent developments in nonequilibrium thermodynamics indicate that in a system far from thermal equilibrium the minute asymmetries could get amplified to generate large scale macroscopic asymmetries. Thus it is possible that macroscopic asymmetries in the universe are direct consequences of microscopic asymmetries. Current developments in elementary particle physics suggest that the observed baryon-antibaryon asymmetry in the universe is a result of small violations in CP and the baryon number conservation. Several authors have proposed
that biochemical \( L - D \) stereoselection is caused by parity violations in weak interactions.\(^9\) After the discovery of weak neutral currents much attention is given to this idea\(^2,4\) as the neutral currents could give rise to minute but nonzero difference in the activation energies of the two enantiomers of the same compound. In this work we present a simple exactly soluble model which clearly shows biochemical \( L - D \) stereoselection could result as a spontaneous breaking of symmetry in an nonequilibrium process.

1.1 Model

It is generally believed that life originated in primeval oceans containing dissolved organic compounds formed by the action of solar ultraviolet radiation or electrical discharges on the primitive atmosphere.\(^5,7\) As there are no significant right-left distinguishing factors in the chemical or geophysical environment, we assume that the prebiotic medium was a racemic mixture of 'basic chemical building blocks of life' (eg, amino acids) and stereoselection occurred after the development of self-replicating molecules. At the initial stages both \( L \) and \( D \) isomers of primitive self-replicating molecules would have existed in comparable concentrations. These molecules use compounds in the prebiotic medium of the correct type (\( L \) or \( D \)) as food and regenerate molecules of the same type. However, because of the difference in activation energies resulting from neutral currents, the rate constants of replication \( K_L \) and \( K_D \) for the two types of molecules will not be exactly equal. Again the self-replicating molecules of one type could interact with the other type inhibiting growth mutually. Perhaps the mixed polymers formed with \( L \) and \( D \) molecules cannot undergo replication. If \( N_L \) and \( N_D \) are the concentrations of the two types of self-replicating molecules, the rate equations governing their evolution can be written in the form,

\[
\frac{dN_L}{dt} = K_L N_L - aN_L N_D \\
\frac{dN_D}{dt} = K_D N_D - aN_D N_L
\]

(1)

where, \( a = \) constant and \( K_L, K_D \) are the replication constants of the two types of molecules. In the presence of neutral currents \( K_L \) is not exactly equal to \( K_D \) and before considering the asymmetric equations with \( K_L \neq K_D \) we consider the symmetric equations with \( K_L = K_D = K \). If we impose the symmetric initial condition \( N_L = N_D, \ t \to \infty \), the equation (1) with \( K_L = K_D = K \) has a symmetric solution,

\[
N_L = N_D = K (a + abe^{-Kt})
\]

(2)
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and two asymmetric solutions, where $b$ is a constant.

$$
N_L = Ae^{kt} \left[ 1 - e^{-\left(\frac{aA}{K}\right)e^{Kt}} \right]^{-1}
$$

or

$$
N_D = Ae^{kt} \left[ 1 - e^{-\left(\frac{aA}{K}\right)e^{Kt}} \right]^{-1}
$$

$$
N_L = Ae^{kt} e^{-\left(\frac{aA}{K}\right)e^{Kt}} \left[ 1 - e^{-\left(\frac{aA}{K}\right)e^{Kt}} \right]^{-1}
$$

The symmetric solution and the two asymmetric solutions are plotted in Figure 1 and the phase trajectories are shown in Figure 2. In the first asymmetric solution $N_L \to \infty$, $N_D \to 0$ as $t \to \infty$, the reverse happens in the second asymmetric solution. Stability analysis shows that the symmetric solution become unstable once the equilibrium concentration $N_L = N_D = K/a$ is reached and bifurcate into one of the stable solution. Clearly the model exhibits spontaneous breaking of L – D symmetry. However, this is ineffective in generating the required stereoselection. Points in the medium, where the symmetry is broken in one sense would occur with equal probability as the places where the symmetry is broken in the opposite sense. Nevertheless a difference in $K_L$ and $K_D$ however small is sufficient to ensure the survival of the two isomers. If $K_L > K_D$ the appropriate solution of (1) is,

$$
N_L = N_0 e^{K_L t} \\
N_D = N_0 e^{K_D t} e^{-aN_0/k e^{Kt}}
$$

The solution (5) is sketched in Figure 3. It is seen that once the concentration of $L$ and $D$ isomers reach a value comparable to the equilibrium concentration an unstability develops and

$$
N_L \to \infty, N_D \to 0 \text{ as } t \to \infty.
$$

We have ignored the diffusion of interacting molecules. In the actual situation, diffusion plays an important role in determining the spatio-temporal distribution of the reaction products. When diffusion is included into (1) we obtain the equations

$$
\frac{\partial N_L}{\partial t} = KN_L - aN_L N_D + b\nabla^2 N_L
$$

$$
\frac{\partial N_D}{\partial t} = KN_D - aN_D N_L + b\nabla^2 N_D
$$
Figure 1: The plot of $N_1 = \frac{N_1}{N_2}$ or $N_2 = \frac{N_2}{N_1}$ versus $t$

(a) Symmetric solution where $N_1 = N_2$.
(b) Asymmetric solution where $N_1 = \frac{N_1}{N_2}$.
(c) Asymmetric solution where $N_1 \to 0$.
Figure 2: Phase trajectories showing the unstability of the symmetric solution.
The analytical solution of the coupled three dimensional partial differential equations (6) is exceedingly difficult. However, it is possible to show that in the one dimensional case solutions of (6) exhibits spontaneous breaking of the homogeneity of the spatial distribution of L and D isomers. If $K_L > K_D$, the colonies containing $N_L$ would predominate and expand.

Kondepodi and Nelson\textsuperscript{3} have shown that in models of the above type bifurcation takes place only if $[K_L - K_D]$ exceeds a lower limit and neutral current effects could produce a sufficiently large difference in $K_L$ and $K_D$.

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