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ORIGINAL PAPER

Frank model with limited resources

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Abstract The classical Frank's autocatalytic kinetic model for the transformation of an almost racemic into a homochiral system assumes that the amount of the achiral substrate from which the enantiomers are formed is time-independent. We show that for the validity of the basic features of the Frank model, this restriction is not necessary.

Keywords Chirality · Homochirality (of biomolecules) · Frank model · Autocatalysis

Mathematics Subject Classification Primary 80A30; Secondary 92E20

1 Introduction

A problem, that for a long time is tantalizing scholars interested in the origin of life, is the fact that the biomolecules in all presently existing life forms (on our planet) are homochiral, i.e., only one of their two possible enantiomers is present in almost exclusive excess.

The two forms of a chiral molecule (the enantiomers) have identical (or almost identical [1]) physical and chemical properties. Thus, for the understanding of homochirality of biomolecules, it needs to be explained

(i) how (and why) some preference of one enantiomer over the other happened, and
(ii) how (and why) this "some preference" evolved into an 100 % excess of the dominant form.

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A vast amount of research on both questions (i) and (ii) was done so far. Recently significant progress has been achieved, both theoretically (see [1–3] and the references cited therein) and experimentally (see [4–6] and the references cited therein).

In this paper we will be concerned with some aspects of the problem (ii).

A widely cited and much examined chemical mechanism for the transformation of an almost racemic into a homochiral system is the model put forward by Frank in 1953 [7]. It consists on a pair of irreversible autocatalytic reactions in which enantiomers are formed, coupled with a reaction in which these combine and disappear from the system. If the enantiomers are denoted by R and S, then the kinetic scheme of the Frank mechanism is:

$$\begin{aligned} A + R &\xrightarrow{k_1} 2R \\ A + S &\xrightarrow{k_1} 2S \\ R + S &\xrightarrow{k_2} \text{products} \end{aligned} \tag{1}$$

where A denotes an achiral reactant. In what follows we shall conveniently refer to A as to the "food".

If the time-dependent amounts of R, S, and A are denoted by $r = r(t)$, $s = s(t)$, and $a = a(t)$, then the time-evolution of the Frank model is described by the system (2) of non-linear differential equations

$$\begin{aligned} \frac{dr}{dt} &= k_1\, a\, r - k_2\, r\, s \\ \frac{ds}{dt} &= k_1\, a\, s - k_2\, r\, s \end{aligned} \tag{2}$$

Within the original Frank model [7], a is considered to be a constant, i.e., time-independent. If so, then the solution of (2) is immediate:

$$\begin{aligned} r(t) &= r_0\,(r_0 - s_0)(r_0 - s_0\, F)^{-1}\, e^{k_1\, at} \\ s(t) &= s_0\,(r_0 - s_0)\, F\,(r_0 - s_0\, F)^{-1}\, e^{k_1\, at} \end{aligned}$$

where we $r_0 = r(0)$, $s_0 = s(0)$, and

$$F = exp\left[-\frac{k_2}{k_1\, a}\,(r_0 - s_0)\, e^{k_1\, at}\right]$$

and where it assumed that $r_0 > s_0$.

The main property of the Frank model is that provided $r_0 > s_0$, no matter how small the difference $r_0 - s_0$ is, the system evolves towards an R-homochiral terminal state, i.e.,

$$\lim_{t\to\infty} r(t) > 0 \quad \text{and} \quad \lim_{t\to\infty} s(t) = 0. \tag{3}$$

There are two evident objections against the plausibility of the Frank model [7]. First,

$$\lim_{t\to\infty} r(t) = \infty \tag{4}$$

which is physically impossible. This weak point could be amended by modifying and slightly extending the original mechanism (1) [8,9].

The second shortcoming is the assumption that the amount of the available food, i.e., a, remains constant, in spite of the fact that it is consumed (in an exponentially increasing manner) by the dominant enantiomer. It may even be doubted that the essence of the Frank model, relations (3), would be lost if the the amount of available food would be limited. In what follows, we show that this is not the case, and that the (modified) Frank model with limited resources maintains its basic property, namely that it transforms the system from an almost racemic initial into a homochiral terminal state.

2 Frank model with limited food

Denote the initial amount of food by $a(0) = a_0$ and assume that during the process (1) no more food (A) enters the system. Then the parameter $a = a(t)$ is time-dependent and

$$\frac{da}{dt} = -k_1\, a\, (r + s). \tag{5}$$

whereas the Eq. (2) remain valid.

From (2) we get

$$\frac{d(r-s)}{dt} = k_1\, a\, (r - s)$$

directly implying

$$r - s = (r_0 - s_0)\, exp\left[k_1 \int_0^t a(t)\, dt\right]. \tag{6}$$

We thus see that if $r_0 > s_0$, then at any moment it will be $r(t) > s(t)$ and thus also in the limit $t \to \infty$, $r(t) > 0$.

Now, at $t \to \infty$, the amount of food will vanish, i.e., $a(t) \to 0$. Then it will be

$$r(k_1\, a - k_2\, s) \to 0$$
$$s(k_1\, a - k_2\, r) \to 0$$

which, because of $r > 0$, yields $s(t) \to 0$. In other words, the main property (3) of the original Frank model is maintained.

In addition, the problem (4) automatically disappears, since it must be $r(t) \leq r_0 + a_0 < \infty$. This, in turn, implies that the integral $\int_0^\infty a(t)\, dt$ has a finite value.

3 Frank model with constant production of food

In this section we consider a somewhat more plausible variant of the Frank model, in which there is a constant production of food A. Then instead of Eq. (5) we have

$$\frac{da}{dt} = -k_1\, a\, (r + s) + \alpha. \tag{7}$$

Two cases need to be examined separately.

Case 1. $\int_0^\infty a(t)\,dt < \infty$

The finiteness of $\int_0^\infty a(t)\,dt$ implies $a(t) \to 0$ for $t \to \infty$. Therefore $dr/dt \to 0$ i.e., $r(k_1\,a - k_2\,s) \to 0$. Because of (6), $r(t) > 0$. Thus

$$k_1\,a(t) - k_2\,s(t) \to 0 \quad \text{i.e.,} \quad s(t) \to \frac{k_1}{k_2}\,a(t) \to 0$$

and the relations (3) remain valid. Also in this case no problem of type (4) is encountered.

Case 2. $\int_0^\infty a(t)\,dt = \infty$

This time, according to (6), in the limit $t \to \infty$ it will be $r(t) \to \infty$. If α is finite, then for a sufficiently large value of t, the right-hand side of (7) will become negative-valued. Thus, the amount of food will begin to decrease.

If $a(t) \to 0$, then using the same reasoning as in the previous case, we conclude that conditions (3) hold, and we are done.

Consider, therefore, the case when $a(t) \to a_\infty$ and $0 < a_\infty < \infty$. Since $r(t) \to \infty$, then for sufficiently large t, the right-hand side of

$$\frac{ds}{dt} = s(k_1\,a - k_2\,r) \tag{8}$$

will become negative-valued, i.e. the amount of the enantiomer S will begin to decrease, attaining a finite limit value. Thus, for sufficiently large t, the amount of S will become constant, and therefore $ds(t)/dt \to 0$. Then, according to (8), it must be $s(t) \to 0$. Conditions (3) are satisfied, although in Case 2 the problem (4) has not been overcome.

From both Cases 1 and 2 we conclude that the Frank model in which a constant production of food is permitted, leads to a homochiral terminal state. This, by the way, means that Frank's the original assumption $a(t) = const$ was irrelevant for the success of his kinetic model of spontaneous chiral stereoselction.

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