Mono- and Bistable Mixtures of Interacting Antipodes

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The evolution of mixtures of interacting antipodes (e.g. chiral, sexual or elementary particle antipodes), in the absence of higher than second order reactions and biased influences, is studied by integrating the rate equation

$$\frac{\mathrm{d}}{\mathrm{d}t}(n\,x) = e + n\left[f_1\,x + f_2(1-x)\right] + n^2\left[g_1\,x^2 + g_2\,x(1-x) + g_3(1-x)^2\right],$$

where x and (1-x) are the relative amounts of the antipodes and n is the total amount, for constant n and q, where $q=1-4s\,\tau/n$ with $s=e+nf_2+n^2\,g_3\ge 0$ and $\tau=1/n(g_1-g_2+g_3)$. x remains stationary if $\tau=\infty$. Monostability, i.e. evolution towards $x=\frac{1}{2}$, results if q<0 or q>1, and bistability, i.e. evolution towards $x=\frac{1}{2}(1\pm\sqrt{q})$ for the initial conditions $x\ge \frac{1}{2}$, respectively, if 0< q<1. Evolution towards $x=\frac{1}{2}(x=0,1)$ for $\tau<0$ ($\tau>0$) results if q=1.

Sequential mergers of systems with x = 0, 1 and unequal sizes may in cases explain why, even without biased influences, there often exists only one of the antipodes in our present world.

In some regions of the island Moorea, 10 miles to the west of Tahiti, all the spiral shells of the land snail *Partula suturalis* are dextral, in others they are sinistral [1]. This is because courtshipping of pairs with opposite chirality is unsuccessful, the penis missing the genital aperture of the partner: If two populations with different chirality mix, the members of the smaller population will only in proportion to the square of their smaller number courtship successfully and will thus die out after some generations.

In trying to treat this phenomenon mathematically and in a broader context, I chose to formulate and integrate a rate equation which has six terms on the r.h.s., four of which are zero in the above case. This equation reads

$$\frac{d}{dt}(nx) = e + n [f_1 x + f_2(1-x)] + n^2 [g_1 x^2 + g_2 x (1-x) + g_3 (1-x)^2]$$
 (1)

and is to describe the evolution of any mixture of antipodes (e.g. chiral, sexual or elementary particle antipodes) if higher than second order reactions and biased antipodal influences are absent. Here x and (1-x) are the relative amounts of the antipodes and n is the total amount. The six rate coefficients can

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depend on n, t, and also on x(1-x) since then their values do not change if in (1) x and 1-x are interchanged. The sum of e, nf_2 and n^2g_3 must be positive or zero because something absent (case x=0) can appear but cannot disappear. The other three coefficients can be positive, zero or negative without any restriction.

In 1953 Frank [2] has proposed a mechanism which amplifies a slight deviation from equipartition $(x = \frac{1}{2})$ of optical antimers, this leading to homochirality (x = 0, 1). Essential in his proposal are eliminating pairwise encounters of the antipodes. This he described by the rate equation

$$\frac{d}{dt}(n x) = n f_1 x + n^2 g_2 x (1 - x)$$
 (2)

with positive f_1 and negative g_2 . In many later publications on the subject, e.g. [3]-[8], it is the negative term $n^2 g_2 x (1-x)$ which brings about the amplification, i.e. the evolution towards x = 0 or x = 1. Equation (1) includes this case.

In order to look for the consequences of (1), it shall be assumed that

$$n = \text{const.}$$
 (3)

This assumption is not unrealistic if one thinks of "saturated" systems, i.e. systems of constant size which contain the maximum possible population under given and constant external and internal

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conditions. By adding

$$\frac{\mathrm{d}}{\mathrm{d}t}[n(1-x)] = e + n[f_1(1-x) + f_2x] + n^2[g_1(1-x)^2 + g_2x(1-x) + g_3x^2]$$

to (1) and putting dn/dt = 0 one obtains

$$f_1 = -2(e/n) - f_2 - n[g_1 + g_3 - 2(g_1 - g_2 + g_3) x(1 - x)].$$
(4)

Before going on with the treatment of the rate equation, the dependence of f_1 on x given by (4) shall be discussed for three special cases:

(i)
$$f_1 = -n q_1 [1 - 2x(1-x)]; q_1 > 0.$$

In this case, if f_1 stands for deaths only, the number of births per unit time of the two species together is $n^2g_1[x^2+(1-x)^2]$. If g_1 is constant, this number is for x=0, 1 twice that for $x=\frac{1}{2}$. Therefore the mean life time $-f_1^{-1}$ for x=0, 1 must be half that for $x=\frac{1}{2}$ if n is to be constant, as indeed results from $f_1=-ng_1[1-2x(1-x)]$: Starvation reduces the mean life time of both species when the number of births per unit time increases.

(ii)
$$f_1 = -n q_2 2x (1-x)$$
; $q_2 < 0$.

This yields $f_1 = 0$ for x = 0, 1 and $f_1 = -\frac{1}{2} n g_2$ for $x = \frac{1}{2}$. Here f_1 is the sum of two rate coefficients, which correspond to the autocatalytic production of the species and that part of the decay of the species which does not take place via the "lethal" encounters with antipodes. For x = 0, 1 the latter channel is dried out and f_1 must be zero if n is to be constant.

(iii)
$$f_1 = -n g_3 [1 - 2x(1 - x)]; g_3 > 0.$$

In this case, if g_3 is constant, the same discussion holds as in case (i).

Insertion of (4) into (1) yields the rate equation for constant n

$$\tau^{-1} dt = \left[\frac{1}{4} (1 - q) - \frac{1}{2} (3 - q) x + 3x^2 - 2x^3\right]^{-1} dx$$
(5)

with

$$\tau = 1/(ng_1 - ng_2 + ng_3) \tag{6}$$

and

$$q = 1 - 4s \, \tau/n, \tag{7}$$

where

$$s = e + nf_2 + n^2 q_3 \ge 0. (8)$$

In order to perform the integration of the r.h.s. of (5) one has to assume that

$$q = \text{const.},$$
 (9)

which is certainly true if s = 0 (q = 1). By using the identity

$$\begin{bmatrix} \frac{1}{4}(1-q) - \frac{1}{2}(3-q)x + 3x^2 - 2x^3 \end{bmatrix}^{-1}
= q^{-1} \left[\frac{2}{x - \frac{1}{2}} - \frac{1}{x - \frac{1}{2}(1 - \sqrt{q})} - \frac{1}{x - \frac{1}{2}(1 + \sqrt{q})} \right], \tag{10}$$

one obtains

$$x = \frac{1}{2} \left\{ 1 \pm q^{1/2} \left[1 - a \exp(-q z) \right]^{-1/2} \right\}$$
 (11)

with

$$z = \int_{0}^{t} \tau^{-1} dt'.$$
 (12)

As for the integration constant a in (11), two cases have to be distinguished:

(i)
$$q > 0$$
.

According to (5), the function dx/dt has two extrema:

$$\frac{\mathrm{d}}{\mathrm{d}x} \left(\frac{\mathrm{d}x}{\mathrm{d}t} \right) = 0 \quad \text{for} \quad x = \frac{1}{2} \left(1 \pm \sqrt{q/3} \right). \tag{13}$$

On chosing the origin of time such that

$$x = \frac{1}{2} (1 \pm \sqrt{q/3})$$
 for $t = 0$,

(11) becomes

$$x = \frac{1}{2} \{ 1 \pm q^{1/2} [1 + 2 \exp(-q z)]^{-1/2} \}.$$
 (14)

Asymptotic forms of (14):

$$x \approx \frac{1}{2} \{1 \pm (a/2)^{1/2} \exp(az/2)\}$$
 for $az < -1$, (15)

$$x \approx \frac{1}{2} \{ 1 \pm q^{1/2} [1 - \exp(-qz)] \}$$
 for $qz > 1$. (16)

On chosing the origin of time such that x = 0, 1 for t = 0, (11) becomes

$$x = \frac{1}{2} \{ 1 \pm q^{1/2} [1 - (1 - q) \exp(-qz)]^{-1/2} \}.$$
 (17)

Asymptotic form of (17):

$$x \approx \frac{1}{2} \{ 1 \pm q^{1/2} [1 + \frac{1}{2} (1 - q) \exp(-qz)] \}$$

for $qz > 1$. (18)

(ii)
$$q < 0$$
.

On chosing the origin of time such that x = 0, 1 for t = 0, (11) becomes

$$x = \frac{1}{2} \{ 1 \pm |q|^{1/2} [(1+|q|) \exp(|q|z) - 1]^{-1/2} \}.$$
 (19)

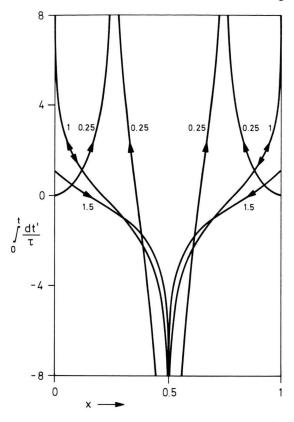


Fig. 1. Dependence of the relative amount x of an antipode on the time t according to (14) and (17) for three positive values of q as defined by (7). The arrows indicate the direction of the evolution.

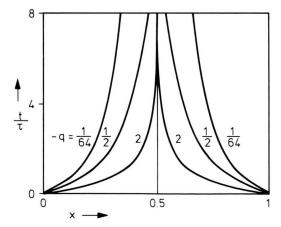


Fig. 2. Dependence of the relative amount x of an antipode on the time t according to (19) for three negative values of q as defined by (7). τ is positive.

Asymptotic form of (19):

$$x \approx \frac{1}{2} \{ 1 \pm [|q|/(1+|q|)]^{1/2} \exp(-\frac{1}{2}|q|z) \}$$

for $|q|z > 1$. (20)

The equations (14) and (17), which hold for q > 0, are illustrated in Fig. 1 for three values of q. If q < 1, τ is positive, if q > 1 it is negative, and if q = 1 it may be positive or negative (cf. (7)). The corresponding different directions of the evolution are indicated by arrows in Fig. 1. Curves for three negative values of q as obtained from (19) are shown in Fig. 2. Here τ is always positive.

In the case q = 1, i.e. s = 0 the r.h.s. of (5) can be integrated without bothering about τ , which means that a time dependence of τ is allowable. For the sake of this case the time integral has been left standing in Fig. 1.

If $q \neq 1$, q depends on $s\tau$, and since it is very improbable that $s \sim 1/\tau$ one has to assume that s and τ are constant separately in order to enable the integration of the r.h.s. of (5). Therefore in Fig. 2 the time integral has been replaced by t/τ .

The results as to the mono- and bistability of the mixtures can be summarized as follows:

The relative amount x of an antipode remains stationary if $\tau = \infty$. Monostability, i.e. evolution towards $x = \frac{1}{2}$, results if q < 0 or q > 1, and bistability, i.e. evolution towards $x = \frac{1}{2} (1 \pm \sqrt{q})$ for the initial conditions $x \ge \frac{1}{2}$, respectively, if 0 < q < 1. If q = 1, the mixture evolves towards $x = \frac{1}{2}$ for $\tau < 0$ and towards x = 0.1 for $\tau > 0$.

During the evolution of the world the bistability of certain mixtures of antipodes interacting according to q = 1 and $\tau > 0$ may have lead to regions where x = 1, and other regions where x = 0, one kind being perhaps a little more frequent than the other one due to biased influences, resulting e.g. from the electroweak interaction (cf. [6]-[8]). If the populations of two such regions merge at a certain time, it is decisive which of the two is the bigger one. Let be $x_A = 1$ in a region A with the population n_A and $x_B = 0$ in a region B with the population n_B . If these populations mix, the resulting x-value will be at first $x_0 = n_A/(n_A + n_B)$ and will evolve to x = 1, 0 for $x_0 \ge \frac{1}{2}$, respectively. Successive merges of this kind may have lead to the extinction of certain antipodes in our known world, its features in this respect seeming to be the result of fortuitous historical events rather than of a physical necessity.

From the knowledge of the equilibrium compositions of bistable antipodal mixtures follows $\tau > 0$ and the value of the product $s \tau/n$. If the mixture is monostable there follows that either $\tau < 0$ or $s \tau/n > \frac{1}{4}$. Observation of the evolution of antipodal mixtures would give information about the values of s and τ separately. The interesting question, however, which specific rate coefficients are involved, can only be answered by studying the interactions themselves, as has been done in the case of Partula

suturalis, where $g_1 > g_2$ follows already from the existence of the stable homochiralities but only careful laboratory observations of the courtshipping of these snails [9] could prove that $q_2 = 0$.

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- [1] cf. J. Murray and B. Clarke, Proc. Roy. Soc. London B, **211**, 83 (1980).
- [2] F. C. Frank, Biochim. Biophys. Acta 11, 459 (1953).
 [3] F. F. Seelig, J. Theor. Biol. 34, 197 (1972).
 [4] P. Decker, J. Mol. Evol. 4, 49 (1974).
- [5] M. Mangel, Phys. Rev. A24, 3226 (1981).
- [6] St. F. Mason, Nature London 311, 19 (1984); Chem. Br. 21, 538 (1985).
- K. Tennakone, Chem. Phys. Lett. 105, 444 (1984).
- [8] D. K. Kondepudi and G. W. Nelson, Physica **125A**, 465 (1984); Nature London **314**, 438 (1985).
- [9] C. S. Lipton and J. Murray, Malacologia 19, 129 (1979).