

Novel rate equations describing isochronous chemical reactions

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Abstract A simple mathematical model involving two first-order Ordinary Differential Equations (ODEs) with fourth-degree polynomial nonlinearities is introduced. The initial-value problem for this system of two ODEs is solved in terms of elementary functions: for an *open* set of initial data, this solution is *isochronous*, i.e., completely periodic with a fixed period (independent of the initial data); in the complementary set of initial data, it blows up at a finite time. This system is likely to be of applicative interest: for instance it models the time evolution of two chemical substances in a spatially homogeneous situation, provided this evolution is characterized by six appropriate chemical reactions whose rates are simply expressed in terms of three a priori arbitrary parameters, or alternatively by five appropriate reactions whose rates are simply expressed in terms of two a priori arbitrary parameters.

Keywords Oscillatory chemical reactions · Rate equations · Isochronous systems

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1 Introduction

Recently we investigated systems of evolutionary nonlinear Ordinary Differential Equations (ODEs) amenable to neat mathematical treatment (including, in some cases, the explicit solution of their initial-value problem) and yielding time evolutions exhibiting *oscillatory* phenomena, possibly including *periodicity* and even *isochrony* or *asymptotic isochrony*: see [1] and other papers referred to there, and, for a review of previous work, the monograph [2]. Models of this kind possibly describing chemical reactions (or other phenomena) and, some of them, characterized by the *isochronous* phenomenology, have been recently introduced and discussed in [3] and [4]. In this paper we report another model of this kind, involving two first-order Ordinary Differential Equations (ODEs) with fourth-degree polynomial nonlinearities. The initial-value problem for this system of two ODEs is solved in terms of elementary functions: for an *open* set of initial data, this solution is *isochronous*, i.e., completely periodic with a fixed period (independent of the initial data, provided they are inside the isochrony region). Otherwise the time evolution of the dependent variables, while always formally periodic with the same period, features instead singularities: if the initial data are on the boundary of the isochrony region, both dependent variables eventually diverge, while if they are outside that region, only one of the two dependent variables becomes (periodically) divergent. This system is likely to be of applicative interest: for instance it models the time evolution of two chemical substances (and possibly of other background chemicals present in such abundance that the fluctuations of their concentrations can be neglected) in a homogeneous, that is, a well-mixed, system. This evolution is characterized by six appropriate chemical reactions whose rates are simply expressed in terms of three a priori arbitrary parameters, or alternatively by five appropriate reactions whose rates are simply expressed in terms of two a priori arbitrary parameters.

The possibility that chemical reactions display an *oscillatory* time evolution is of course well known; for a terse review of mathematical treatments of these phenomena see the introduction to our previous papers [3] and [4], and especially the references quoted there and reported again here [5–13].

Our new model is treated in the following section, an explanation of how this model was arrived at is provided in Appendix A, and a terse discussion of its relation to known isochronous systems of analogous type [14] is provided in Appendix B. A brief last section entitled “Outlook” completes the paper.

2 A novel isochronous model

In this section we report our model, we exhibit the solution of the corresponding initial-value problem and we tersely describe its behavior. Although the fact that this solution satisfies the equations characterizing the evolution of this model could be checked by direct (if somewhat cumbersome) computations, we also considered appropriate to explain (in Appendix A) how this solvable model was arrived at, providing thereby an alternative way to check its solution.

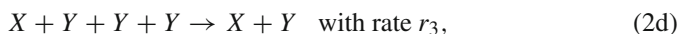
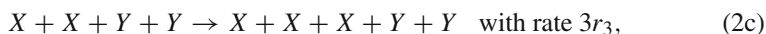
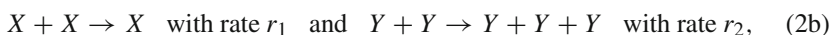
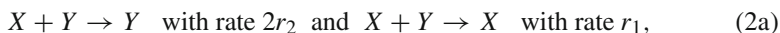
The relevant evolution ODEs read as follows:

$$\dot{X} = -\omega X \left[2(Y/\bar{Y}) + X/\bar{X} - 3(X/\bar{X})(Y/\bar{Y})^2 \right], \quad (1a)$$

$$\dot{Y} = \omega \left\{ \bar{Y} - Y \left[X/\bar{X} - Y/\bar{Y} + (X/\bar{X})(Y/\bar{Y})^2 \right] \right\}. \quad (1b)$$

Here $X \equiv X(t)$ and $Y = Y(t)$ are the dependent variables (representing in appropriate units the concentrations of the two chemicals), t is the independent variable (“time”) and (here and throughout) superimposed dots indicate differentiations with respect to it, while ω , \bar{X} , \bar{Y} are three a priori arbitrary *positive* constants, the first of which, ω , has the dimensions of inverse time and sets the time scale, and the other two, \bar{X} and \bar{Y} , correspond clearly to the equilibrium configuration of the model.

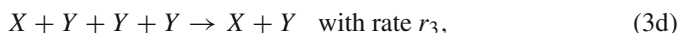
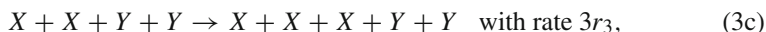
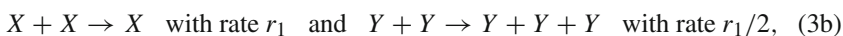
Note that these rate equations do not feature any term in their right-hand sides having a *negative* coefficient and not being proportional to the dependent variable whose evolution they describe raised to a *positive* power, the presence of which would mar their applicative interpretation (see, for instance, the discussion of this point in [4]). Indeed all terms in the right-hand sides of these two ODEs are proportional to the dependent variable whose evolution they describe, raised to a *positive* power: first and second power for the first ODE describing the evolution of $X(t)$, first, second and third power for the second ODE describing the evolution of $Y(t)$; except for the first term in the right-hand side of the second equation, which is, however, positive and therefore allows a natural interpretation as incoming flux. In fact a possible chemical interpretation of this model is to assume that these two ODEs describe—in addition to an incoming flux into the system, with constant rate $\omega\bar{Y}$, of the chemical Y (see the first term in the right-hand side of 1b)—the following six chemical reactions:



where the three a priori arbitrary rates r_1 , r_2 and r_3 are clearly related to the parameters ω , \bar{X} and \bar{Y} as follows:

$$r_1 = \omega/\bar{X}, \quad r_2 = \omega/\bar{Y}, \quad r_3 = \omega/(\bar{X}\bar{Y}^2) = r_1 r_2^2 / \omega^2. \quad (2e)$$

Moreover, if one restricts attention to the case with $\bar{Y} = 2\bar{X}$ entailing $r_1 = 2r_2$, then an alternative chemical interpretation of the model corresponds—in addition again to an incoming constant flux into the system of the chemical Y with constant rate $\omega\bar{Y}$ —to the following five chemical reactions:



where now the, a priori arbitrary, rate r_1 is related as above to the parameters ω and \bar{X} , while clearly $r_3 = r_1^3 / (4\omega^2)$.

Of course in the initial and final states of each of the above reactions there might appear other chemicals, provided their abundance is so large that the variations of their concentrations due to these chemical reactions are negligible.

The general solution of the system (1) reads as follows:

$$X(t) = \bar{X} \frac{A \cos [2(\omega t - \varphi)] + \sqrt{R(t)}}{R(t)}, \tag{4a}$$

$$Y(t) = \bar{Y} \frac{-A \cos [2(\omega t - \varphi)] + \sqrt{R(t)}}{1 + A \sin [2(\omega t - \varphi)]}, \tag{4b}$$

with

$$R(t) = 1 + A^2 + 2 A \sin [2(\omega t - \varphi)]. \tag{4c}$$

Here A and φ are two a priori arbitrary constants, only restricted by the inequalities $A > 0$ and $0 \leq \varphi < \pi/2$. The assignments

$$A = \frac{[4(1 - X_0 Y_0)^2 + X_0^2 (1 - Y_0^2)^2]^{1/2}}{X_0 (1 + Y_0^2)}, \tag{5a}$$

$$\varphi = \frac{1}{2} \arcsin \left(\frac{X_0 (1 + Y_0^2)^2 - 4Y_0}{(1 + Y_0^2) [4(1 - X_0 Y_0)^2 + X_0^2 (1 - Y_0^2)^2]^{1/2}} \right), \quad 0 \leq \varphi < \pi/2, \tag{5b}$$

where

$$X_0 = \frac{X(0)}{\bar{X}}, \quad \text{and} \quad Y_0 = \frac{Y(0)}{\bar{Y}}, \tag{5c}$$

entail that (4) yield the solution of the initial-value problem. It is plain that these solutions are periodic with period

$$T = \frac{\pi}{\omega}, \tag{6}$$

and that they are *nonsingular* (and always *positive*, thereby allowing a “chemical” significance) throughout their time evolution provided the initial data entail that $0 \leq A < 1$ (clearly $A = 0$ corresponds to the equilibrium configuration, $X(t) = \bar{X}$, $Y(t) = \bar{Y}$); while for $A = 1$ clearly both $X(t)$ and $Y(t)$ diverge at $t = (\varphi + \pi/2) / \omega \bmod (T)$, and for $A > 1$ only the dependent variable $Y(t)$ diverges at these times.

We report in Figs. 1 and 2 two graphs displaying a representative example of the behavior of the solution (4).

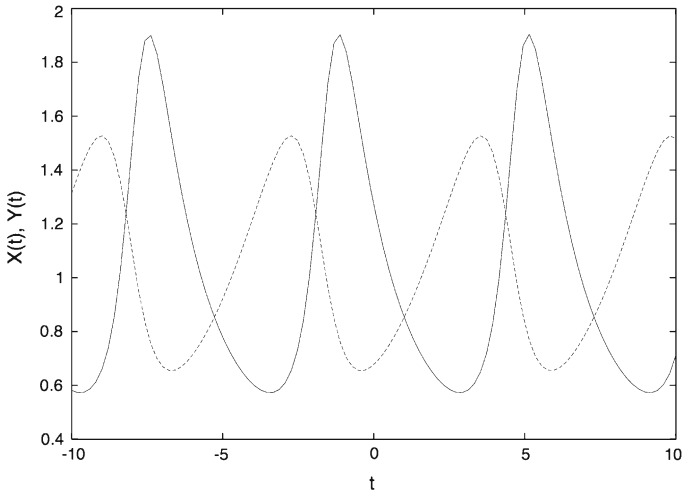


Fig. 1 The solution $X(t)$ (solid line) and $Y(t)$ (dotted line) of (1) given by (4). The parameters have the following values: $\bar{X} = \bar{Y} = 1$, $\omega = 1$, $A = 0.4$ and $\phi = 0$

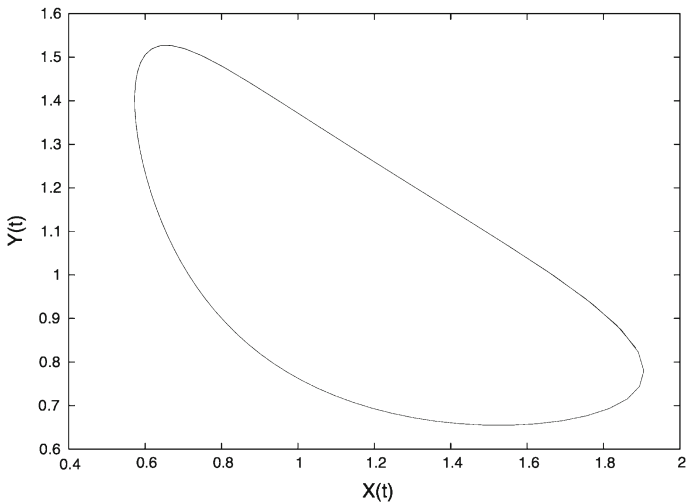


Fig. 2 The periodic orbit in the XY plane described by the solution (4) of (1). The parameters have the following values: $\bar{X} = \bar{Y} = 1$, $\omega = 1$, $A = 0.4$ and $\phi = 0$

3 Outlook

The specific chemical (or other) applications of the mathematical model described in this paper exceed our competence. If and when they emerge it shall be appropriate to complement the analytical results reported above with numerical simulations, and also with (both analytical and numerical) investigations of the behavior of our model when the reaction rates fail to satisfy *exactly* the conditions on their values implied by our treatment.

Let us end by mentioning that presumably, using techniques analogous to those employed in this paper and in the previous one [4], additional systems of two ODEs suitable to model chemical reactions might be obtained. But we trust that these models would generally be rather more complicated than that presented herein, including in particular a considerably larger number of chemical reactions the rates of which would be required to satisfy, in order to yield isochrony, a considerably larger number of relations among them than those presented above (see the relevant discussion in Appendix B).

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A How this model was arrived at

Our starting point is the following single first-order ODE:

$$\zeta' = -\frac{\omega}{2}\zeta^3, \quad \zeta \equiv \zeta(\tau). \tag{A.1a}$$

Hereafter we shall consider both the dependent variable ζ and the independent variable τ to be *complex* numbers, and (here and below) primes denote differentiations with respect to the variable τ . The constant ω is instead assumed, throughout, to be a priori arbitrary, but *real* (indeed, for definiteness, *positive*).

Clearly the solution of the initial-value problem for this ODE is

$$\zeta(\tau) = \left\{ \omega\tau + [\zeta(0)]^{-2} \right\}^{-1/2}. \tag{A.1b}$$

We now “isochronize” this ODE, via the following standard [2] change of dependent and independent variables:

$$z(t) = \exp(i\omega t)\zeta(\tau), \quad \tau = \frac{\exp(2i\omega t) - 1}{2i\omega}, \tag{A.2a}$$

clearly entailing

$$\tau(0) = 0, \quad \dot{\tau} = \exp(2it), \quad \dot{z} = i\omega z + \exp(3it)\zeta'(\tau), \tag{A.2b}$$

hence, via (A.1a),

$$\dot{z} = \omega \left(iz - \frac{1}{2}z^3 \right). \tag{A.3}$$

Here and below i is the standard imaginary unit, $i^2 = -1$.

Next, let us introduce the real and imaginary parts of $z(t)$:

$$z(t) = x(t) + i y(t). \quad (\text{A.4})$$

Then the complex ODE (A.3) becomes the following system of two first-order ODEs:

$$\dot{x} = \omega \left[-y - \frac{x}{2} (x^2 - 3y^2) \right], \quad (\text{A.5a})$$

$$\dot{y} = \omega \left[x + \frac{y}{2} (y^2 - 3x^2) \right]. \quad (\text{A.5b})$$

Next, we perform the following change of dependent variables:

$$x^2(t) = X(t)/\bar{X}, \quad y(t) = x(t) Y(t)/\bar{Y}, \quad (\text{A.6})$$

introducing thereby the two a priori arbitrary constants \bar{X} and \bar{Y} . It is thereby easily seen that the two new dependent variables $X(t)$ and $Y(t)$ evolve precisely according to our system (1).

We can now also easily obtain the general solution (4) of our system (1). Indeed clearly from (A.2) and (A.1b) we get

$$z(t) = \left\{ \frac{1 - \exp(-2i\omega t)}{2i} + [z(0)]^{-2} \exp(-2i\omega t) \right\}^{-1/2}, \quad (\text{A.7})$$

or, equivalently,

$$z(t) = \sqrt{2} \{-i + A \exp[-2i(\omega t - \varphi)]\}^{-1/2}, \quad (\text{A.8a})$$

where we used the assignment

$$i + 2[z(0)]^{-2} = A \exp(2i\varphi), \quad (\text{A.8b})$$

with A positive and $0 \leq \varphi < \pi/2$. This entails, from (A.4) and (A.6) (all at $t = 0$), the expressions (5a) and (5b) of A and φ .

Then, from (A.4), (A.6) and (A.8a) (now at time t), one gets

$$\frac{Y(t)}{\bar{Y}} = \frac{y(t)}{x(t)} = \tan \arg [z(t)] = -\tan \left[\frac{\operatorname{arccot} \sigma(t)}{2} \right] \quad (\text{A.8c})$$

where

$$\sigma(t) = \frac{A \cos [2(\omega t - \varphi)]}{1 + A \sin [2(\omega t - \varphi)]}, \quad (\text{A.9})$$

entailing

$$\frac{Y(t)}{\bar{Y}} = -\sigma(t) + \sqrt{1 + [\sigma(t)]^2} \tag{A.10}$$

hence (4b).

Likewise, from (A.4) and (A.6) one gets

$$\text{Re} \left[z^2(t) \right] = [x(t)]^2 - [y(t)]^2 = \left[X(t)/\bar{X} \right] \left\{ 1 - [Y(t)/\bar{Y}]^2 \right\}, \tag{A.11}$$

and via (A.10) this yields (4a).

B Relation to known isochronous systems of analogous type

In this Appendix we discuss tersely the relation of the dynamical system discussed in this paper to analogous isochronous systems reported in the classic review paper by Chavarriga and Sabatini [14].

All isochronous systems of the following type,

$$\dot{x} = y + F(x, y), \quad \dot{y} = -x + G(x, y), \tag{B.1a}$$

with $F(x, y)$ and $G(x, y)$ homogeneous polynomials of third degree,

$$F(x, y) = \sum_{n=0}^3 f_n x^n y^{3-n}, \quad G(x, y) = \sum_{n=0}^3 g_n x^n y^{3-n}, \tag{B.1b}$$

have been identified and investigated [14]. They belong, in their canonical version, to the following four classes (see Tables 5 and 6 in Sect. 11 of [14]):

$$\dot{x} = -y + x^3 - 3xy^2, \quad \dot{y} = x + 3x^2y - y^3, \tag{B.2a}$$

$$\dot{x} = -y + x^3 - xy^2, \quad \dot{y} = x + x^2y - y^3, \tag{B.2b}$$

$$\dot{x} = -y + 3x^2y, \quad \dot{y} = x + 9xy^2 - 2x^3, \tag{B.2c}$$

$$\dot{x} = -y - 3x^2y, \quad \dot{y} = x - 9xy^2 + 2x^3. \tag{B.2d}$$

It is easily seen that the first of these 4 isochronous systems coincides with (A.5) (with $\omega = 1$) via the replacement $x \mapsto \sqrt{2}y, y \mapsto -\sqrt{2}x$.

It is now useful to review tersely the development (see Appendix A) that allowed us to go from (A.5) to (1), which, for the convenience of this discussion, is reported here in the dimensionless version with $\omega = \bar{X} = \bar{Y} = 1$:

$$\dot{X} = -X \left(2Y + X - 3XY^2 \right), \quad \dot{Y} = 1 - Y \left(X - Y + XY^2 \right). \tag{B.3}$$

The need to make such a transition is due to the fact that the system (A.5) is clearly unsuitable to fit with our applicative context, due to the negative coefficient in the first

term in the right-hand side of (A.5a), as well as the fact that the isochronous solution rotating around the center at $x = y = 0$ entails that the variables $x(t)$ and $y(t)$ change sign through their evolution.

The first observation is that this system, in addition to the equilibrium configuration at $x = y = 0$, clearly features a second equilibrium configuration at $x = y = 1$. This, as well as the “defect” of equation (A.5a) mentioned above, suggests replacing the y dependent variable via the assignment

$$Y(t) = \frac{y(t)}{x(t)}, \quad y(t) = x(t) Y(t), \quad (\text{B.4})$$

whereby the system (A.5) becomes

$$\begin{aligned} \dot{x} &= -x \left[Y + \frac{x^2}{2} (1 - 3Y^2) \right], \\ \dot{Y} &= 1 + Y \left[Y - x^2 (1 + Y^2) \right]. \end{aligned} \quad (\text{B.5})$$

This is now a system of rate equations suitable for applications; however, its structure suggest to replace the dependent variable $x(t)$ with $X(t) = x^2(t)$, and this yields (B.3), the isochronous solution of which rotate now around the equilibrium configuration $X = Y = 1$.

A natural question that now arises is whether an analogous treatment could be made for the other three isochronous systems (B.2). But the answer is negative, because—as it can be easily verified—none of them features equilibrium configurations for which both dependent variables, x and y , are real and nonvanishing (so that—if need be, by appropriate sign changes—the equilibrium values of these variables could be both brought to lie inside the first quadrant of the xy Cartesian plane).

Incidentally, it can be easily checked that the same observation also applies to the isochronous systems with quadratic nonlinearities reported in [14], which have been the basis of the treatment in our previous paper [4], where, to arrive at isochronous systems of rate ODEs suitable for applications, we had to use a different, considerably more cumbersome, approach, consisting in the performance of an affine transformation of the dependent variables and a subsequent check that the ODEs thereby obtained feature equilibria in the first Cartesian quadrant as well as coefficients satisfying the positivity requirements required to allow applicative interpretations.

One might now wonder whether an analogous approach to that of [4] could yield acceptable findings when applied to the systems (B.2) (or to other isochronous systems reported in [14]). But even if the answer were positive, the applicative systems thereby obtained would feature many more non-vanishing terms in their right-hand sides (out of the 20 terms to be generically expected, corresponding to two non homogeneous polynomials of degree three in two variables), and would therefore be much less likely to be experimentally realizable than the system introduced in this paper (see in particular, in Sect. 2, the discussion of the applicability of our model (1)).

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