



# Using the blow-up technique for a modified Lindemann mechanism

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## Abstract

We study a modified Lindemann mechanism, in which the second part of the reaction is  $2B \rightarrow P$  instead of  $B \rightarrow P$ . This model gives rise to a degenerate singularity in the associated system of ordinary differential equations. Using the blow-up technique, we describe this singularity qualitatively, showing that there is an invariant line, and that in the first quadrant (where the reaction takes place), it is stable. As a consequence, numerical methods for integrating differential equations can be used with confidence. Several examples are included.

**Keywords** Lindemann mechanism · Mass action · Ordinary differential equation · Blow-up · Stability

**Mathematics Subject Classification** 92E20 · 34E10 · 34M35

## 1 Introduction

The classical Lindemann Mechanism (LM) states that if a reactant  $A$  decays into a product  $P$  by colliding with itself, the chemical reaction is expressed as:



This classical mechanism has been studied by many authors, and its mathematical properties have been explored in [1]. Fraser [2] has used it as an example in his work on the dynamical systems approach to chemical kinetics. Calder [3] studies several properties about stability, unicity, concavity and asymptotic behaviour.

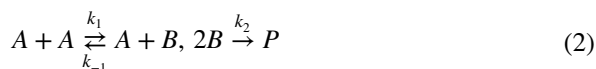
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There exist different modifications to the basic scheme (see [4–6]). We study the following innovative version of the LM:



where  $k_1$ ,  $k_{-1}$ , and  $k_2$  are the reaction rate constants. Application of the law of mass action gives the system of ordinary (non linear) differential equations that the concentrations of  $A$ ,  $B$  and  $P$  must verify:

$$\begin{aligned} \frac{da}{d\tau} &= k_{-1}ab - k_1a^2 \\ \frac{db}{d\tau} &= k_1a^2 - k_{-1}ab - 2k_2b^2 \\ \frac{dp}{d\tau} &= k_2b^2 \end{aligned} \quad (3)$$

where  $\tau$  is time and we the initial conditions are:  $a(0) = a_0$ ,  $b(0) = 0$ ,  $p(0) = 0$  (traditionally, the complex and product are not initially present). The following conservation law holds:

$$a(\tau) + b(\tau) + 2p(\tau) = a_0 \quad (4)$$

After simplifying, we obtain the planar reduction of system (3):

$$\begin{aligned} \frac{da}{d\tau} &= k_{-1}ab - k_1a^2 \\ \frac{db}{d\tau} &= k_1a^2 - k_{-1}ab - 2k_2b^2 \end{aligned} \quad (5)$$

which, rescaling the variables as follows:

$$t = k_2\tau, \quad x = \frac{k_1}{k_2}a, \quad y = \frac{k_1}{k_2}b, \quad \varepsilon = \frac{k_{-1}}{k_1}, \quad \sigma = \frac{k_2}{k_1} \quad (6)$$

becomes the dimensionless planar system:

$$\begin{aligned} \frac{dx}{dt} &= \varepsilon xy - x^2 \\ \frac{dy}{dt} &= x^2 - \varepsilon xy - 2\sigma y^2 \end{aligned} \quad (7)$$

which has a single equilibrium point at  $(0, 0)$  whose Jacobian matrix is null. This is a degenerate singularity, for which the classical methods are unsuitable. We study the dynamical properties of system (7) using the blow-up technique [7]. This technique allows us to study the long-term behavior of the reaction and to show that there is an asymptotic power series “infinitely tangent” to the trajectories of (7), despite the degeneracy of the singularity. We compute some terms of this power series and give a method for computing any approximation.

In the end, all the qualitative study performed by means of the blow-up technique allow us to ensure that the traditional numerical algorithms for computing solutions of ODEs can be confidently used for this modified Lindemann model. In chemical settings, we may mention specifically the methods developed in [8–10]. We include some examples.

## 2 Study of the equilibrium point of $X$

The vector field  $X$  defined by (7) has a single singularity (equilibrium point) at  $(x, y) = (0, 0)$ , as is easily verified. The Jacobian matrix at the origin is the zero matrix because the order of  $X$  (the least of the degrees of its monomials) is 2. This implies that we cannot use its linearization to study the local behaviour of its trajectories near  $(0, 0)$ . We are going to use the well-known blowing-up technique [7] which, as we are going to show, will completely clarify the situation. In order to clarify the exposition, we shall denote  $P(x, y) = \varepsilon xy - x^2$  and  $Q(x, y) = x^2 - \varepsilon xy - 2\sigma y^2$ . The fact that  $P(x, y)$  and  $Q(x, y)$  are both homogeneous of the same degree 2 will simplify our arguments considerably.

In what follows, we are going to show plots of the vector field  $X$  after assigning the values  $k_1 = 1, k_2 = 0.4, k_{-1} = 0.2$ , which give  $\varepsilon = 0.2, \sigma = 0.4$ .

### 2.1 Tangent cone

First of all, we need to compute the *tangent cone* at  $(0, 0)$  of the vector field  $X$ . This tangent cone is defined as the set of zeroes of the homogeneous polynomial  $C(x, y) = yP(x, y) - xQ(x, y)$ :

$$T \equiv (yP(x, y) - Q(x, y) = 0) \equiv (ex^2y + exy^2 + 2sxy^2 - x^3 - x^2y = 0) \quad (8)$$

which can be factorized as

$$T \equiv (x(y - ax)(y - bx) = 0) \equiv L_{OY} \cup L_a \cup L_b, \quad (9)$$

where  $L_{OY}$  is the  $OY$ -axis and  $L_a, L_b$  are the lines  $y - ax = 0, y - bx = 0$ , respectively, and where  $a, b$  are given by

$$a = \frac{1 - \varepsilon + \sqrt{\varepsilon^2 + 2\varepsilon + 8\sigma + 1}}{2(\varepsilon + 2\sigma)}, \quad b = \frac{1 - \varepsilon - \sqrt{\varepsilon^2 + 2\varepsilon + 8\sigma + 1}}{2(\varepsilon + 2\sigma)} \quad (10)$$

so that, as  $\varepsilon, \sigma \geq 0$  and  $\varepsilon + \sigma > 0$ , we always have  $a > 0, b < 0$ . Thus,  $L_a$  is included in the first quadrant for  $x \geq 0$  and  $L_b$  in the fourth one for  $x > 0$ . The lines  $L_{OY}, L_a$  and  $L_b$  are represented as the projective points (in the real projective line)  $[0 : 1], [1 : a]$  and  $[1 : b]$  in homogeneous coordinates  $[u : v]$ .

## 2.2 The vertical axis

We study the behaviour of  $X$  “near” the vertical axis  $OY$ . To this end, we perform the blowing-up of  $(0, 0)$  with local equations

$$\begin{cases} x = \bar{x}\bar{y} \\ y = \bar{y} \end{cases} \quad (11)$$

which transforms  $X$  into the vector field

$$\bar{X} = ((\varepsilon + 2\sigma)\bar{x}\bar{y} + (\varepsilon - 1)\bar{x}^2\bar{y} - \bar{x}^3\bar{y})\frac{\partial}{\partial \bar{x}} + (-2\sigma\bar{y}^2 - \varepsilon\bar{x}\bar{y}^2 + \bar{x}^2\bar{y}^2)\frac{\partial}{\partial \bar{y}} \quad (12)$$

This vector field has an obvious invariant line  $\bar{y} = 0$  which can be factored out in order to study the singularity, giving:

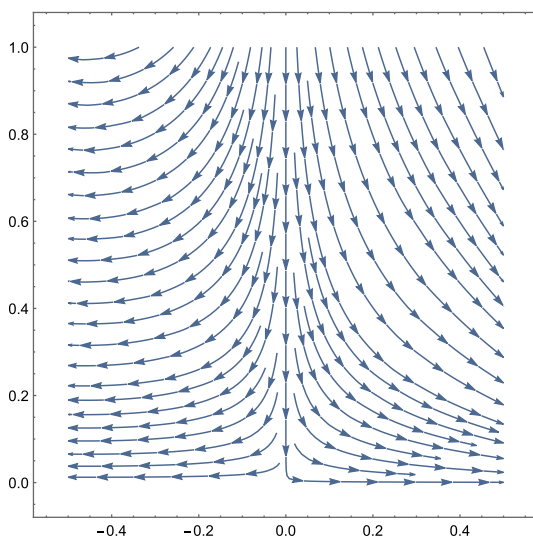
$$\bar{X}_{OY} = ((\varepsilon + 2\sigma)\bar{x} + (\varepsilon - 1)\bar{x}^2 - \bar{x}^3)\frac{\partial}{\partial \bar{x}} + (-2\sigma\bar{y} - \varepsilon\bar{x}\bar{y} + \bar{x}^2\bar{y})\frac{\partial}{\partial \bar{y}} \quad (13)$$

which has the following Jacobian (at  $(0, 0)$ , corresponding to the vertical axis in the blow-up):

$$J_{OY} = \begin{pmatrix} \varepsilon + 2\sigma & 0 \\ 0 & -2\sigma \end{pmatrix} \quad (14)$$

which, as  $\varepsilon, \sigma > 0$  (and we may assume they are both rational), corresponds to a hyperbolic singularity. Its flow for  $\varepsilon = 0.4$ ,  $\sigma = 0.2$  (for instance) is shown in Fig. 1, for  $\bar{y} > 0$  (which is the physically “feasible” part). It is clear how the the line  $\bar{x} = 0$

**Fig. 1** Flow of the singularity of  $\bar{X}_{OY}$



[which in this coordinates corresponds to the line  $L_{OY}$  in the  $(x, y)$  plane] is invariant, as is the other axis  $\bar{y} = 0$ , and the hyperbolic structure is also evident in the plot.

As a consequence, the vertical line  $L_{OY}$ , given by  $y = 0$  is invariant for  $X$  [this was evident from the local equation of  $X$  near  $(0, 0)$ ] but no trajectory of  $X$  accumulates at  $(0, 0)$  in the direction of the axis  $L_{OY}$ . This is the main property we need regarding the point  $[u : v] = [0 : 1]$  of the tangent cone.

As a final remark, the singularity corresponding to  $L_{OY}$  is then unstable (for  $\bar{y} > 0$ ): apart from the invariant axis,  $\bar{x} = 0$ , any other trajectory of  $\bar{X}_{OY}$  starting at  $\bar{y}(0) > 0$  exits any neighbourhood of  $(0, 0)$  after a finite time.

### 2.3 The line $L_a \equiv y - ax = 0$

Next we study the line  $L_a$  which, for  $x > 0$  is included in the first quadrant, as explained above. We perform the blow-up given by the equations

$$\begin{cases} x = \bar{x} \\ y = \bar{x}(\bar{y} - a) \end{cases} \quad (15)$$

and, after dividing once by  $\bar{x}$ , obtain the vector field

$$\begin{aligned} X_{L_a} = & \left( \varepsilon \left( \frac{\sqrt{(\varepsilon+1)^2 + 8\sigma} - \varepsilon + 1}{2(\varepsilon+2\sigma)} + \bar{y} \right) - 1 \right) \bar{x} \frac{\partial}{\partial \bar{x}} \\ & - \left( \sqrt{(\varepsilon+1)^2 + 8\sigma} + \varepsilon\bar{y} + 2\sigma\bar{y} \right) \bar{y} \frac{\partial}{\partial \bar{y}} \end{aligned} \quad (16)$$

which, notably, has two invariant lines:  $\bar{x} = 0$  (this is the exceptional divisor) and  $\bar{y} = 0$ . This second invariant line for  $X_{L_a}$  implies that the line  $y = ax$  is also invariant for the original vector field  $X$ . Thus:

**Lemma 1** *The vector field  $X$  has the separatrix (invariant manifold)  $y = ax$ .*

The linear part of  $X_{L_a}$  is given by the Jacobian matrix

$$J_{L_a} = \begin{pmatrix} -1 + \varepsilon \frac{1 - \varepsilon + \sqrt{(\varepsilon+1)^2 + 8\sigma}}{2(\varepsilon+2\sigma)} & 0 \\ 0 & -\sqrt{(\varepsilon+1)^2 + 8\sigma} \end{pmatrix} \quad (17)$$

whose eigenvalues are, obviously, the nonzero elements on its diagonal, call them  $\lambda_1$  and  $\lambda_2$ . The second one,  $\lambda_2 = -\sqrt{(\varepsilon+1)^2 + 8\sigma}$  is always strictly negative (recall that both  $\varepsilon$  and  $\sigma$  are non-negative real numbers). Using Mathematica's `Reduce` method, we obtain that  $\lambda_1$  is never zero for  $\varepsilon, \sigma \geq 0$ . An easy argument shows that the quotient  $\lambda_1/\lambda_2$  is irrational when  $\sqrt{(\varepsilon+1)^2 + 8\sigma}$  is so. In any case, we obtain

**Lemma 2** *The singularity at  $(\bar{x}, \bar{y}) = (0, 0)$  of  $X_{L_a}$  is a stable focus for  $\bar{y} \geq 0$  whose only non-singular separatrices are  $\bar{x} = 0$  and  $\bar{y} = 0$ . If  $\sqrt{(\varepsilon+1)^2 + 8\sigma}$  is irrational, then those are the only separatrices. Otherwise, there is an open set  $U \subset \bar{x} \geq 0$  such*

that for any  $(\bar{x}_0, \bar{y}_0) \in U$ , the trajectory of  $X_{L_a}$  passing through  $(x_0, y_0)$  converges to  $(0, 0)$ , is analytic and is tangent to  $\bar{y} = 0$ .

**Proof** The only part left to be proved is the tangency to  $\bar{y} = 0$ . This happens if the eigenvalue  $\lambda_2$  is greater (i.e. has less absolute value) than  $\lambda_1$ . This can be also checked using Mathematic's Reduce method, taking into account that both  $\varepsilon$  and  $\sigma$  are non-negative.

This provides all the dynamics of the original vector field  $X$  “near” the separatrix  $y = ax$ : all the trajectories near that line approach  $(0, 0)$  as  $t \rightarrow \infty$  tangent to  $y = ax$ . We now need to study  $L_b$  to obtain a full description of the dynamics of  $X$ .

As a matter of fact, the restriction of  $X$  to the  $OX$ -axis:

$$X|_{ox} \equiv P(x, 0) \frac{\partial}{\partial x} + Q(x, 0) \frac{\partial}{\partial y} = -x^2 \frac{\partial}{\partial x} + x^2 \frac{\partial}{\partial y} \quad (18)$$

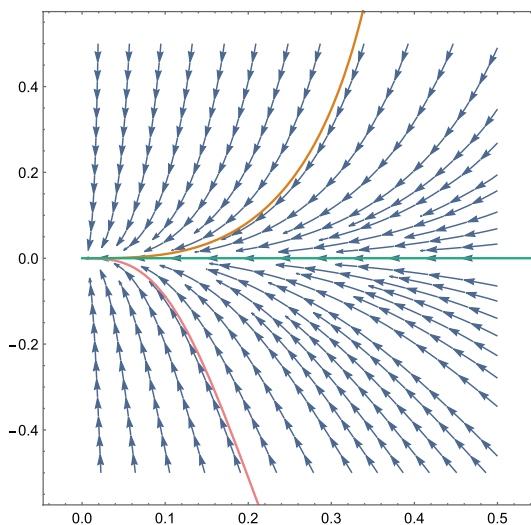
is transversal to  $OX$  everywhere except at  $(0, 0)$  for  $x > 0$  [recall that this is the only part of the  $(x, y)$  plane we have to study, as both variables design concentrations]. We know that  $b < 0$  always, so that the dynamics of  $X$  on  $x, y > 0$  have already been completely studied, as the line  $y = bx$  does not meet the first quadrant. However, for the sake of completeness and to rule out any strange behaviour, we proceed to study the vector field near  $L_b$ .

Figure 2 shows the local structure of  $X_{L_a}$  for the specific values of  $\varepsilon = 0.2, \sigma = 0.4$ .

## 2.4 The line $L_b \equiv y = bx$

When we blow-up  $X$  using the map

**Fig. 2** Flow of  $X_{L_a}$  near  $(\bar{x}, \bar{y}) = (0, 0)$ , with its separatrix  $\bar{y} = 0$  and two trajectories,  $\varepsilon = 0.2, \sigma = 0.4$



$$\begin{cases} x = \bar{x} \\ y = \bar{x}(\bar{y} - b) \end{cases} \quad (19)$$

we obtain the following vector field

$$X_{L_b} \equiv \frac{\left( \varepsilon \left( -\sqrt{(\varepsilon+1)^2 + 8\sigma} + \varepsilon(2\bar{y} - 1) + 4\sigma\bar{y} - 1 \right) - 4\sigma \right)}{2(\varepsilon + 2\sigma)} \bar{x} \frac{\partial}{\partial \bar{x}} + \left( \sqrt{(\varepsilon+1)^2 + 8\sigma} - y(\varepsilon + 2\sigma) \right) \bar{y} \frac{\partial}{\partial \bar{y}} \quad (20)$$

whose singularity at  $(0, 0)$  corresponds to the projective point  $[1 : b]$ , that is the line  $y = bx$  in the plane  $(x, y)$ . Its Jacobian is

$$J_{L_b} = \begin{pmatrix} \frac{-\varepsilon^2 - \varepsilon\sqrt{(\varepsilon+1)^2 + 8\sigma} - \varepsilon - 4\sigma}{2(\varepsilon + 2\sigma)} & 0 \\ 0 & \sqrt{(\varepsilon+1)^2 + 8\sigma} \end{pmatrix} \quad (21)$$

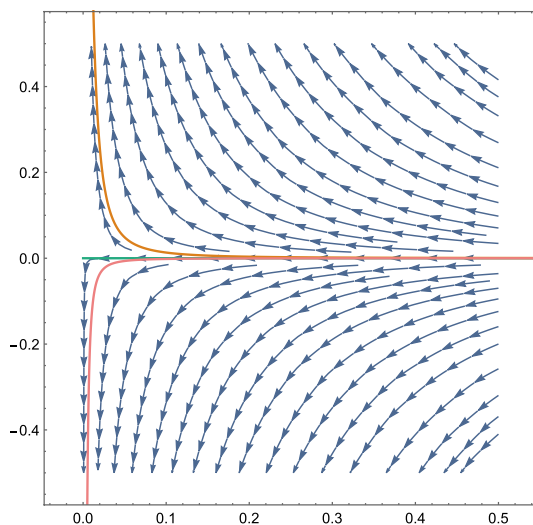
and, as  $\varepsilon, \sigma > 0$ , its eigenvalues are real of different sign. Hence,  $(0, 0)$  corresponds to a hyperbolic singularity of  $X_{L_b}$ , which is then unstable. Figure 3 shows the local structure of  $X_{L_b}$  for  $\bar{x} > 0$  near  $(0, 0)$  for the same values  $\varepsilon = 0.2, \sigma = 0.4$ .

## 2.5 Local dynamics near $(x, y) = (0, 0)$

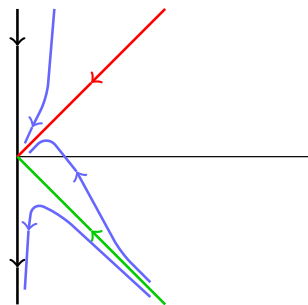
In summary, the dynamics of the vector field  $X$  given by (7) can be schematized as in Fig. 4. Specifically:

1. The  $OY$  axis is invariant, and any trajectory starting at  $(0, y_0)$  converges to  $(0, 0)$ .

**Fig. 3** Flow of  $X_{L_b}$  near  $(\bar{x}, \bar{y}) = (0, 0)$ , with its separatrix  $\bar{y} = 0$  and two trajectories,  $\varepsilon = 0.2, \sigma = 0.4$



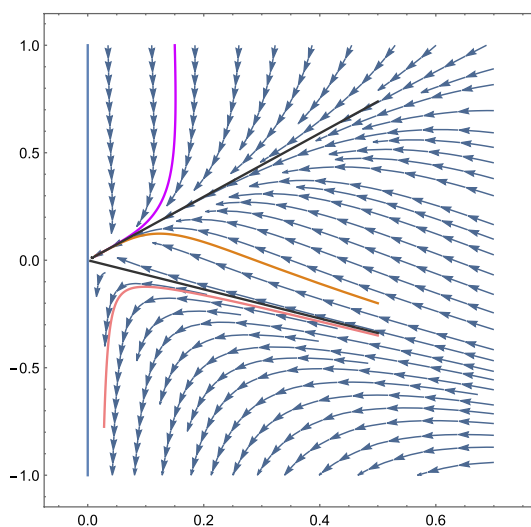
**Fig. 4** Schematics of the dynamics of (7) near  $(0, 0)$



2. There is a single invariant line  $y = ax$ , with  $a > 0$ , on which  $X$  flows towards  $(0, 0)$ .
3. Any trajectory starting at  $(x_0, y_0)$  with  $y_0 > ax_0$  converges to  $(0, 0)$  tangent to  $y = ax$  from above.
4. The  $OX$  axis is not invariant, any trajectory starting at  $(x_0, 0)$  enters the first quadrant and stays there, and converges to  $(0, 0)$  tangent to  $y = ax$  from below.
5. There is an invariant line  $y = bx$  with  $b < 0$ , on which  $X$  flows towards  $(0, 0)$ .
6. Any trajectory of  $X$  starting at  $(x_0, y_0)$  with  $bx_0 < y_0 < 0$  crosses the  $OX$  axis after a finite time.
7. Any trajectory of  $X$  starting at  $(x_0, y_0)$  with  $y_0 < bx_0$  diverges to  $(0, -\infty)$  tangent to  $OY$ .

So, any specific realization of (7) for any  $\varepsilon, \sigma > 0$  will provide a reasonable model for the general  $X$ . Figure 5, contains the plot of  $X$  for  $\varepsilon = 0.2, \sigma = 0.4$ .

**Fig. 5** The vector field (7) for  $\varepsilon = 0.2, \sigma = 0.4$ . Separatrices in black. In magenta, yellow and red, three typical trajectories





## 2.6 Power series expansion

Using the technique of the Newton-Puiseux polygon [11, 12], we can construct the formal generalized power series expansion of the solutions of  $X$ . Namely:

**Lemma 3** *Let  $X$  be the vector field defined by (7). Then any generalized power series starting with  $y = ax$ , solving it has the form*

$$y(x) = ax + kx^\mu + \sum_{i=0}^{\infty} a_i(k)x^{\mu(i+1)-1} \quad (22)$$

where  $k$  is an arbitrary constant,  $a(k, i)$  is a constant depending on  $k$  and  $i$ , and finally,  $\mu$  is given by:

$$\mu = \frac{\varepsilon^2 - \varepsilon\sqrt{(\varepsilon+1)^2 + 8\sigma} - 4\sigma\left(\sqrt{(\varepsilon+1)^2 + 8\sigma} - 1\right) + \varepsilon}{\varepsilon\left(\sqrt{(\varepsilon+1)^2 + 8\sigma} + \varepsilon + 1\right) + 4\sigma} \quad (23)$$

which is always greater than 1 for  $\varepsilon, \sigma > 0$ . Furthermore, the power series is “convergent” in the following sense: for any  $k$  there are  $C, R > 0$  such that

$$|a_i(k)| < CR^{\mu(i+1)-1}. \quad (24)$$

The proof of this result is just a straightforward application of the results of [11, 12], using Mathematica to solve the recurrent equations.

Notice that, in (22),  $k$  is the first term affected by the “initial condition” represented by that generalized power series expansion. The fact that  $\mu > 1$  (which can be verified using Mathematica’s `Reduce` method) implies that all the trajectories are tangent to  $y = ax$  eventually. Of course, all the coefficients further than  $\mu$  are also affected by  $k$ .

For  $\varepsilon = 0.2, \sigma = 0.4$ , we obtain

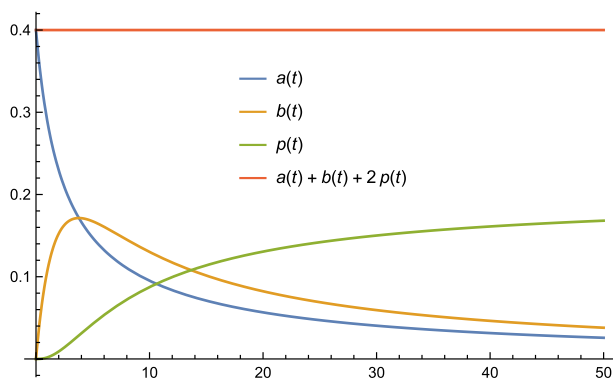
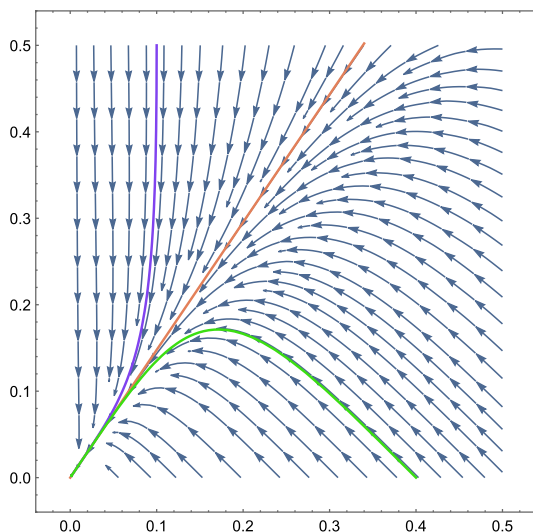
$$\begin{aligned} s(x) = & 1.47703x + 0.74809k^2x^{10.1715} + 0.665812k^3x^{13.2287} + 0.650558k^4x^{16.2859} \\ & + 0.674178k^5x^{19.3431} + 0.727637k^6x^{22.4002} + 0.809098k^7x^{25.4574} \\ & + 0.920447k^8x^{28.5146} + 1.06618k^9x^{31.5718} \\ & + 1.25319k^{10}x^{34.6289} + \dots \end{aligned} \quad (25)$$

## 3 The original equation, and the classical mechanism

What our arguments above prove is that, in the end, the modified Lindemann model given by (3) can be reasonably solved using the standard numerical tools for ordinary differential equations, as the only singular point is completely stable.

Using the same parameters as in the previous section, namely  $k_1 = 1, k_2 = 0.4, k_{-1} = 0.2$ , (3) becomes

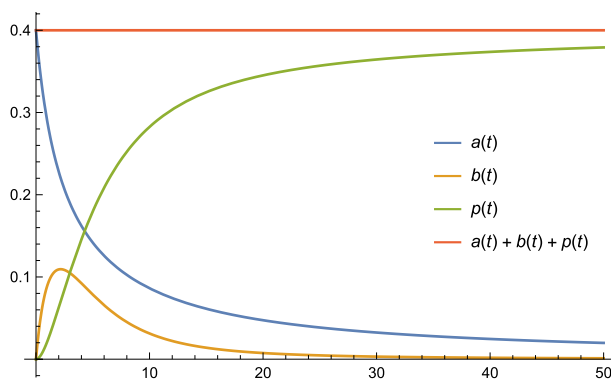
**Fig. 6** Phase portrait  $(a, b)$  of (26). The straight line is the invariant line. The solution below starts at  $(0.4, 0)$ , the solution above at  $(0.1, 0.5)$



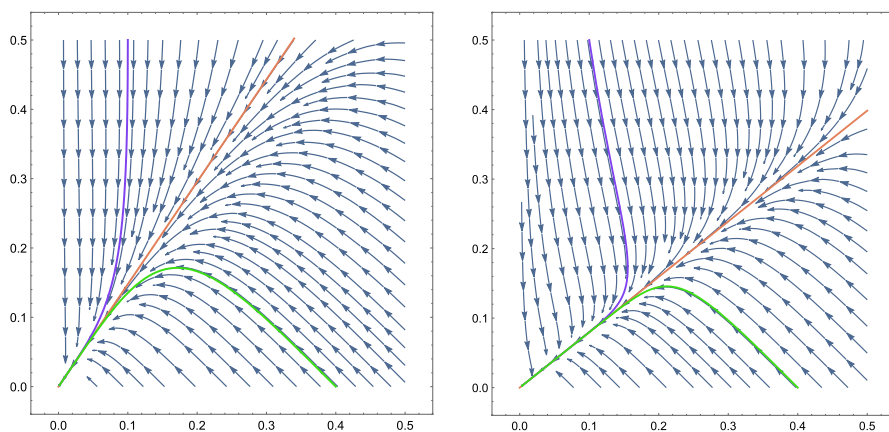
**Fig. 7** Evolution of  $a(t)$ ,  $b(t)$  and  $p(t)$ . The straight line is  $a(t) + b(t) + 2p(t)$ , showing the conservation law (4)

$$\begin{aligned}
 \frac{da}{d\tau} &= 0.2ab - a^2 \\
 \frac{db}{d\tau} &= a^2 - 0.2ab - 0.8b^2 \\
 \frac{dp}{d\tau} &= 0.4b^2
 \end{aligned}
 \tag{26}$$

The equation of the invariant line in the first quadrant for the variables  $(a, b)$  (the variable  $p$  depends on  $b$ ) is  $b = 1.477a$ , and for the initial conditions  $a(0) = 0.4$ ,  $b(0) = 0$ , and  $a(0) = 0.1$ ,  $b(0) = 0.5$ , we obtain the phase portrait in Fig. 6. Looking just at the solution starting at  $a(0) = 0.4$ ,  $b(0) = 0$ , and plotting together  $a(t)$ ,  $b(t)$ ,  $p(t)$  and, we obtain also the conservation law (4), as can be seen in Fig. 7.



**Fig. 8** Classical Lindemann mechanism with same parameters and initial values of  $a, b, p$  (and the conservation Law  $a + b + p = a(0)$ ). Compare with Fig. 7, much slower



**Fig. 9** Phase planes of the Lindemann mechanism for different values of  $k_1, k_2$  and  $k_{-1}$ . Notice the difference in the separatrices and the curvature of the trajectories above them. Left:  $k_1 = 1, k_2 = 0.4, k_{-1} = 0.2$ , right:  $k_1 = 1, k_2 = 0.4, k_{-1} = 0.95$

Notice how the reaction speed is much slower than in the classical Lindemann mechanism, with the same initial values and parameters (Fig. 8). Finally, in order to illustrate the relevance of the separatrix, we compare the phase planes of the modified Lindemann mechanism with the constants  $k_1 = 1, k_2 = 0.4, k_{-1} = 0.2$  and with  $k_1 = 1, k_2 = 0.4, k_{-1} = 0.9$ , in Fig. 9.

## 4 Conclusions

We have introduced a modification of the classical Lindemann Mechanism in which the second part of the reaction is  $2B \rightarrow P$ . When expressed as a system of ordinary differential equations, the equilibrium point turns out to be degenerate, which raises

the question of the effectiveness of the classical numerical algorithms for computing its trajectories.

We prove that the singularity is stable in the domain of the reaction (i.e. concentrations are non-negative real numbers). Even more, we show that there is a separatrix adherent to the singularity, which is actually a straight line. Thus, there is a specific ratio of concentrations of reactants which, if the reaction starts with that ratio, this ratio stays the same during all the reaction.

All the trajectories of the system approach that line asymptotically, and we provide an approximated generalized power series expansion of all the solutions of the differential equation, and show that it has an (explicitly computed) exponent admitting an arbitrary constant as coefficient, and after this term, all the remaining ones are uniquely determined.

Some examples are provided which show the variation of the slope of the separatrix and the common shape of the trajectories.

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