Tourbillion in the Phase Space of the Bray-Liebhafsky Nonlinear Oscillatory Reaction and Related Multiple-Time-Scale Model

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Abstract

The mixed-mode dynamical states found experimentally in the concentration phase space of the iodate catalyzed hydrogen peroxide decomposition (The Bray-Liebhafsky oscillatory reaction) are discussed theoretically in a related multiple-time-scale model, from the viewpoint of tourbillion. With aim to explain the mixed-mode oscillations obtained by numerical simulations of the various dynamical states of a model for the Bray-Liebhafsky reaction under CSTR conditions, the folded singularity points on the critical manifold of the full system and Andronov-Hopf bifurcation of the fast subsystem are calculated. The interaction between those singularities causes occurrence of tourbillion structure.

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1. Introduction

The *tourbillion* is common phenomenon in mixed-mode dynamical states of complex nonlinear reaction systems. It is predicted by mathematicians and recognized in some reaction systems of significant interest for chemical engineers [1–3]. However, although the mathematical explanation could be quite precise, this phenomenon cannot be easily identified in real system. The question arises: What is tourbillion and how shall we recognize it in complex nonlinear reaction systems? In the following we are trying to answer this question analyzing the complex iodate catalyzed hydrogen peroxide decomposition known as the Bray-Liebhafsky (BL) oscillatory reaction [4, 5].

Any reaction system starting from some arbitrary initial conditions tends to final steady or equilibrium state that plays the role of an attractor, passing through distinct regions of the phase space while its different chemical species simultaneously transform through the reaction network. A reaction network may consist of several reaction routes. The competition between them sometimes results in alternating dynamical states of a system during its transformation from initial to final state. This dynamical feature of the considered nonlinear process, known as oscillatory evolution, depends very much on the external conditions. [6], [7] Moreover, the complexity of reaction networks depends on the number of species and reactions between them.

The dimension of an attractor in a phase space is function of the number of independent intermediate species whose concentrations plays a role of variables in mathematical expressions. In almost all real systems that can be described by stoichiometric model, even if they are chemical, biochemical, social or other ones, there are more than three such variables resulting in deep mathematical problems during theoretical analysis of the dynamical states and evolution of the system in function of the external parameters. However, with aim to predict desirable dynamical state, it is rarely necessary to know all details of the reaction mechanism of the analyzed process proceeding under selected conditions. In most cases, without loosing generality, reaction dynamics of an overall process can be considered in lower dimensional phase space where reduced attractors are defined by lower number of variables, that is, in two or three dimensional projection of n-dimensional space, simplifying the initial mathematical models and relevant calculations. [8], [9]

Since, almost all complex many variable dynamical systems are characterized by multiple-time-scales, various forms of attractors and transitions between different dynamical states were studied in such systems, [10]–[14] for example: the Bray-Liebhafsky oscillatory

reaction (first reported homogeneous oscillatory chemical reaction) [4]–[5], [15]–[26] and references cited therein, the Belousov-Zhabotinsky (the most popular one) [27]–[34], the Briggs-Rauscher [35]–[39], the birhythmic Hypothalamic-Pituitary-Adrenal axis dynamics [40]–[42] and references cited therein, the intracellular calcium dynamics [43], the periodic CO oxidation at Pt surfaces [1] and [44], methylen blue oscillator [45]–[47] and references cited therein, chlorite-iodide oscillator [48] and other ones [49].

Thus, already in the first report about the BL reaction, [4] where Bray analyzed dual role of hydrogen peroxide as an oxidizing and reducing agent, the domination of different reaction routes during one reaction process was announced. More precisely, he noticed that the hydrogen peroxide decomposition to water and oxygen in the presence of iodate and hydrogen ions

$$2H_2O_2 \xrightarrow{\ IO_3^-, H^+\ } 2H_2O + O_2,$$ (D)

is the result of the reduction (R) of iodate to iodine and the oxidation (O) of iodine to iodate by the following complex reaction scheme

$$2IO_3^- + 2H^+ + 5H_2O_2 \rightarrow I_2 + 5O_2 + 6H_2O$$ (R)

$$I_2 + 5H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O \ .$$ (O)

Their rates tend to become equal and we usually observe only a smooth decomposition described by reaction (D) where iodine, as intermediate species, does not appear in this stoichiometric relation. However, in a narrow range of concentrations, the alternating domination of processes R and O is also possible resulting in periodic increase and decrease of the iodine concentration during stepwise decrease of the hydrogen peroxide and increase of the oxygen concentrations. This, apparently simple oscillatory reaction, known as the Bray-Liebhafsky one, consists of a complex homogeneous catalytic oscillatory process involving numerous iodine intermediates such as I^-, HIO, HIO_2 and I_2O beside already mentioned iodine (I_2) that all oscillates. [21] The concentrations of mentioned species in the considered process differ for several orders of magnitudes among themselves. Thus, typical concentration of hydrogen peroxide during oscillatory state of the system is between 10^{-2} and 10^{-1}, the concentration of iodine is between 10^{-5} and 10^{-4}, whereas the concentrations of other species are much lower, between 10^{-9} and 10^{-6}. Consequently, their simultaneous time variations are

different, resulting in dissimilar behaviors characteristic of multiple-time-scale systems with, at least, *slow* (*large*-concentration) and *fast* (*low*-concentration) species. In the chemistry, physical chemistry and biochemistry, the slow and fast variables are also known as *external* and *internal* ones, respectively. [50] More precisely, in such range of concentrations the middle concentration species are common. Depending on external conditions, they often can change their properties during reaction from slow to fast ones and *vice versa*, and although they have characteristics of slow or fast variables, we shall identify them as *slow-fast* ones. Particularly, during the smooth decomposition described by reaction (D), iodine is an internal species just as all other intermediary species. However, according to the stoichiometry of reaction pathways R and O, I_2 is an external compound while the other intermediary compounds are internal.

In systems, where concentrations of crucial species differ significantly, the *relaxation oscillations* are common. There, fast variables always quickly adjust to any change in slow variables, which act as the parameters for the fast subsystem. Thus, in a phase space of two slow and several fast variables, the stationary values of fast variables are positioned on the two-dimensional surface in multi-dimensional space. In the domain where relaxation oscillations are present this surface is folded having at least two stable and one unstable branch. It is known as *manifold*. Such a manifold calculated with the studied model can be seen in Fig. 5. Fast variables in that case often alternate between two stable branches resulting in relaxation oscillatory evolution of considered dynamical system.

In singular perturbation theory all variables are usually classified just as slow or fast ones, such that we are dealing, there, with the models having two fast and one slow, or one fast and two slow types of them. These models exhibit different dynamical characteristics. However, dynamical system with two slow and one fast variable can often be rescaled to system with one slow and two fast variables [51] and [52]. Our aim here is just to explain that the considered model is selforganized in such manner that its dynamical states can alternate during the course of reaction, between the ones characteristic for two slow and one fast variable to the others characteristic for one slow and two fast variables (ref. [51], page 22).

In chemical, physicochemical and biochemical nonlinear dynamical systems the multiple-time-scale models consist commonly of three-time scale types of variables. There are, usually, several slow ones (external species, generally, reactants and products), several fast ones (internal species, intermediates) and often a middle one (the slow-fast one) having either internal or external characteristics in different regions of phase space. Necessary condition for such alternations is that some species belong to middle scale in both,

concentration and time scale. Besides, in such reaction systems, two additional kinds of species can appear, both unimportant for present discussion of *mixed-mode oscillations* (MMO-s) and tourbillions. They are (a) *structural control variables* [6] with concentrations that can be considered as constant (*pool approximation*), [53] and (b) *flow through reactants* [54] with very low concentrations that can be considered as being in the steady state during whole process and, therefore, do not entering in reduced differential equations.

Between several models [4], [5], [15], [21], [22], [55]–[64] proposed to describe the above mentioned Bray-Liebhafsky oscillatory reaction, we used here the one given in Table I [61] to explore multiple-time-scale behavior of the BL reaction. First eight reactions, where three of them are reversible, describe the mechanism of the process under batch conditions whereas all of them must be taken into account in an open *continuous stirred tank reactor* (CSTR) where only hydrogen peroxide is the inflow species. (The reaction system can be open with respect to other species, too. However, in that case, the number of intermediate species and related reactions increases importantly resulting in large mathematical problems without essentially important results.) In the model under consideration, where hydrogen peroxide is taken as the only inflow species, there are six independent species: H_2O_2, I_2, I^-, HIO, HIO_2 and I_2O and they are all dynamically important. Thus, mathematically speaking, we are dealing with six-dimensional problem. This model is able to describe almost all features of BL reaction, including regular simple oscillatory evolution, periodic mixed-modes with *large-amplitude oscillations* (LAO-s) and *small-amplitude oscillations* (SAO-s), as well as the chaotic occurrence of LAO-s and SAO-s and their combinations. [65]

In multiple-time-scale systems with more than one slow variable, mixed-mode oscillations may appear in the region with simple sustained oscillations. They generally consist of two types of oscillations with distinct amplitudes: LAOs and SAOs. The LAOs are *global phenomena*, generated by the geometry of the critical manifold having an unstable branch between two stable ones. They are well known as relaxation type dynamics governed by slow sliding of the system over the stable branches of critical manifold, periodically interrupted by much faster jumps from one to another stable branch of this hyper-surface in phase space. These fast jumps usually occur at some special points (*fold* points) of the critical manifold where the stable branch is connected with unstable one.

Table 1. Model of the BL reaction used in numerical simulations [62]

Reaction			Reaction rate[a]	No.
$IO_3^- + I^- + 2H^+$	$\rightleftharpoons$	$HIO + HIO_2$	$r_1 = k_1\,[I^-]$ $r_{-1} = k_{-1}\,[HIO]\,[HIO_2]$	(R1) (R-1)
$HIO_2 + I^- + H^+$	$\longrightarrow$	$I_2O + H_2O$	$r_2 = k_2\,[HIO_2]\,[I^-]$	(R2)
$I_2O + H_2O$	$\rightleftharpoons$	$2HIO$	$r_3 = k_3\,[I_2O]$ $r_{-3} = k_{-3}\,[HIO]^2$	(R3) (R-3)
$HIO + I^- + H^+$	$\rightleftharpoons$	$I_2 + H_2O$	$r_4 = k_4\,[HIO]\,[I^-]$ $r_{-4} = k_{-4}\,[I_2]$	(R4) (R-4)
$HIO + H_2O_2$	$\longrightarrow$	$I^- + H^+ + O_2 + H_2O$	$r_5 = k_5\,[HIO]\,[H_2O_2]$	(R5)
$I_2O + H_2O_2$	$\longrightarrow$	$HIO + HIO_2$	$r_6 = k_6\,[I_2O]\,[H_2O_2]$	(R6)
$HIO_2 + H_2O_2$	$\longrightarrow$	$IO_3^- + H^+ + H_2O$	$r_7 = k_7\,[HIO_2]\,[H_2O_2]$	(R7)
$IO_3^- + H^+ + H_2O_2$	$\longrightarrow$	$HIO_2 + O_2 + H_2O$	$r_8 = k_8\,[H_2O_2]$	(R8)
$(H_2O_2)_{in}$	$\longrightarrow$	H_2O_2	$r_9 = j_0\,[H_2O_2]_{in}$	(R9)
H_2O_2	$\longrightarrow$	$(H_2O_2)_{out}$	$r_{10} = j_0\,[H_2O_2]$	(R10)
I^-	$\longrightarrow$	$(I^-)_{out}$	$r_{11} = j_0\,[I^-]$	(R11)
HIO	$\longrightarrow$	$(HIO)_{out}$	$r_{12} = j_0\,[HIO]$	(R12)
HIO_2	$\longrightarrow$	$(HIO_2)_{out}$	$r_{13} = j_0\,[HIO_2]$	(R13)
I_2O	$\longrightarrow$	$(I_2O)_{out}$	$r_{14} = j_0\,[I_2O]$	(R14)
I_2	$\longrightarrow$	$(I_2)_{out}$	$r_{15} = j_0\,[I_2]$	(R15)

[a] Reaction rate constants at 60°C: $k_1 = 1.383 \times 10^2$ min^{-1}; $k_{-1} = 7.91 \times 10^7$ mol$^{-1} \times$ dm$^3 \times$ min^{-1}; $k_2 = 4.79 \times 10^{10}$ mol$^{-1} \times$ dm$^3 \times$ min^{-1}; $k_3 = 5.00 \times 10^3$ min^{-1}; $k_{-3} = 3.15 \times 10^8$ mol$^{-1} \times$ dm$^3 \times$ min^{-1}; $k_4 = 3.00 \times 10^{11}$ mol$^{-1} \times$ dm$^3 \times$ min^{-1}; $k_{-4} = 46.97$ min^{-1}; $k_5 = 1.487 \times 10^4$ mol$^{-1} \times$ dm$^3 \times$ min^{-1}; $k_6 = 5.00 \times 10^5$ mol$^{-1} \times$ dm$^3 \times$ min^{-1}; $k_7 = 2.00 \times 10^3$ mol$^{-1} \times$ dm$^3 \times$ min^{-1}; $k_8 = 2.2303 \times 10^{-4}$ min^{-1}. In CSTR we distinguish inflow species $(X_i)_{in}$ and outflow species $(X_i)_{out}$. The concentrations of iodate and hydrogen ions, taken as constant in simulations ($[IO_3^-] = 0.0474$ mol $\times$ dm^{-3} and $[H^+] = 0.0958$ mol $\times$ dm^{-3}) are included in corresponding rate constants. The inflow concentration of hydrogen peroxide was $[H_2O_2]_{in} = 0.155$ mol $\times$ dm^{-3}. Flow rate as control parameter is designated as j_0.

However, in mixed-mode, LAOs are mixed with SAOs of different nature. They occur at the fold points as a *local phenomena* generated by some *folded singularities*. In the mixed-mode region we can expect the occurrence of phenomena known as *canards* and *tourbillion*. [14], [51], [66]– [68]

Here particular attention is focused on the dynamical structures that appear in the mixed-mode region of the BL oscillatory reaction in a CSTR: particularly tourbillion as specific time-evolution pattern in one mixed-mode period. Our aim is to explore the selforganization of dynamical states with tourbillion that alternate during the course of reaction, with changes in number of slow and fast variables.

2. Materials and methods

2.1 Experimental

A schematic diagram of the instrumental setup is shown in ref. [69]. The experiments were conducted in the CSTR where inflow concentration of sulfuric acid is a control parameter. Under the following experimental conditions: $[KIO_3]_0 = 0.059$ mol dm^{-3}, $[H_2O_2]_0 = 0.15$ mol dm^{-3}; the specific flow rate $j_0 = 0.0295$ min^{-1}, T = 56 ^{o}C and the inflow concentration of H_2SO_4 varied from 0.0422 mol dm^{-3} to 0.09 mol dm^{-3}. Temporal evolution of the system was followed potentiometrically, by means of a Pt electrode connected to the Ag/AgCl reference electrode.

2.2 Numerical simulations and analysis

We have analyzed time series obtained by numerically simulating the model of the Bray-Liebhafsky oscillatory reaction under isothermal CSTR conditions (T = 60 ^{o}C), Table 1. All calculations were performed using MATLAB program package. System of the ordinary differential equations was solved by means of ode15s solver. Relative and absolute error tolerance values 3×10^{-14} and 1×10^{-20}, respectively, were used in all simulations.

Initial values of concentrations were $[IO_3^-]_0 = 0.0474$ mol $\times$ dm^{-3}, $[H^+]_0 = 0.0958$ mol $\times$ dm^{-3} and $[H_2O_2]_0 = 0.155$ mol $\times$ dm^{-3}. Flow rate j_0 and inflow hydrogen peroxide concentration $[H_2O_2]_{in}$, as control parameters, were varied in wide region of values.

3. Calculations

During typical relaxation oscillations, considered system has two slow (H_2O_2, and I_2 concentrations, although species I_2 is sometimes fast variable) and four fast variables (HIO, HIO_2, I_2O and I^- concentrations). In such system the fast variables are almost always in a nonequilibrium stationary (or steady) state (more precisely: in a quasi steady state). Their steady-state values are determined by the concentrations of the slow variables. In the general case, during one full period of system evolution in the phase space that can consists of one or many oscillations, the concentrations of the slow species change significantly governing the steady state concentrations of fast species in such a manner that they are positioned in one hyper surface or very close to it. The critical manifold of the BL reaction model under consideration is a two- dimensional surface placed in a six-dimensional phase space. It is completely determined by steady-state equations of four fast species. Hence, we have to solve the system of four equations with six variables. Obviously, there is no unique solution in this case, unless we fix two variables. For any pair of fixed values, we will obtain new solution, corresponding to another point on the critical manifold. Hence, we can say that two chosen variables determine the solution in parametric fashion. Moreover, as far as we use same four rate equations for fast species, final solution, the critical manifold, will not depend on our choice of two parametric variables. Therefore, for the reasons of simplicity, instead the more natural parameters: the concentrations of H_2O_2 and I_2, the concentrations of H_2O_2 and HIO are selected to be the parametric variables in our calculations. The points on the manifold are obtained by symbolic calculations (see Appendix).

Points at the *fold line* were determined according to ref. [51], from the condition:

$$\text{Det}(J(X_i)) = 0 ,$$

(1)

where X_i denotes the fast species HIO, HIO_2, I_2O and I^- and J is the Jacobian of corresponding fast subsystem. This request must be fulfilled on the border between stable and unstable branch of the critical manifold. Concentrations of slow species are treated here (in evaluation of the Jacobian for fast subsystem) as they are constant. This assumption seems to be appropriate since they are changing on much slower time scale then the fast ones.

Dynamics of the slow subsystem on the critical manifold can be reduced. Concentrations of all fast species are connected by their steady state equations. It means that if beside two slow ones, one fast variable is known too, the others are also uniquely

determined, even if the critical manifold is folded. Hence, the situation in our system is analogous to dynamical systems with two slow and only one fast species, and therefore, the singularity point on the fold line was calculated according to ref. [51], from the condition:

$$\frac{\mathrm{d}f_1}{\mathrm{d}t} \cdot \frac{\partial g}{\partial x_1} + \frac{\mathrm{d}f_2}{\mathrm{d}t} \cdot \frac{\partial g}{\partial x_2} = 0,$$

(2)

where x_1 and x_2 are concentrations of slow species, f_1 and f_2 are their corresponding rates and g is a rate of the fast variable. In our case this gives for *e.g.* [HIO]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}[H_2O_2]}{\mathrm{d}t}\right) \cdot \frac{\partial}{\partial[H_2O_2]}\left(\frac{\mathrm{d}[HIO]}{\mathrm{d}t}\right) + \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}[I_2]}{\mathrm{d}t}\right) \cdot \frac{\partial}{\partial[I_2]}\left(\frac{\mathrm{d}[HIO]}{\mathrm{d}t}\right) = 0.$$

(3)

Furthermore, two *nullclines* were evaluated from corresponding rate equations for sets of all four fast species combined with each of two slow ones. Hence, we have one nullcline that describe the steady state condition of species I_2, HIO, HIO_2, I_2O and I^- (the iodine nullcline) and the other one for the combination H_2O_2, HIO, HIO_2, I_2O and I^- (the hydrogen peroxide nullcline). Each one of two subsystems gives as a solution a line, located in the critical manifold of the fast species. Steady state of the full system is placed in the point where two nullclines intersect, and it will be shortly referred below as the *equilibrium* (therminology common in mathematical papers), keeping in mind that our system is of non-equilibrium type. More precisely, in our papers this is known as disproportionation steady-state. [61]

Finally, *Andronov-Hopf point* was identified numerically on the iodine nullcline using simple test ensuring that the real part of two complex eigenvalues (corresponding to five dimensional Jacobian) is passing through zero.

4. Results and discussion

4.1 Dynamical structures in mixed mode region

The various dynamical states obtained by numerical simulations of the model for the BL nonlinear reaction system given in Table 1 are presented in Figure 1. Considering the oscillatory region as a function of two external parameters: the flow rate j_0 and hydrogen peroxide concentration in inflow $[H_2O_2]_{in}$ we can see narrow mixed-mode region (between +

and ×) that appear inside phase space, but very close to the upper-right border of the simple sustained oscillations.

More precisely, we can clearly distinct three regions of initial hydrogen peroxide concentrations. In the first one we cannot obtain oscillations for any flow rate; the main steady state is always stable. In other two regions, oscillations can be found for middle values of flow rates, that is, "inside" the curved line in Fig, 1, while outside of these bounds, only stable steady state remains. More precisely, in the second one, we can find only simple sustained oscillations, whereas in the third one we have various kinds of periodic and aperiodic (chaotic) oscillations. In this third region, for the lowest values of the control parameter j_0, there is only stable steady state (Fig. 1). With increase of the flow rate j_0, the stable steady state transforms to the unstable one through supercritical Andronov-Hopf bifurcation, where the stable limit cycle emerges. With further increase of the flow rate j_0, dynamics of the system is featured with different forms of oscillations: simple quasi-sinusoidal oscillations are observed first; they quickly rise in amplitude, changing waveform to that typical for simple relaxation LAO-s. With additional increase of the flow rate, mixed-mode dynamics with complex sequences of both LAO-s and SAO-s emerges, in which the ratio between numbers of SAO-s and LAO-s is increased (Fig. 1, periodic states between + and ×). [65] Finally, mixed-mode oscillations suddenly disappear and only dynamical states with SAO-s rest until second Andronov-Hopf bifurcation where the system reaches the stable steady state once more. All periodic mixed-mode states are separated by chaotic transitions between them. [70]

Numerically obtained oscillations are of the same type as the experimental ones (Fig. 2) consisting of various mixtures of LAO-s and SAO-s. Observability of experimental MMO-s testify that phenomena are robust in spite of rather narrow oscillatory region where they could be found. Moreover, although oscillatory region with or without mixed mode oscillations and chaotic states inside it appear often in narrow region of phase space, lot of natural reaction systems such as many biological ones [40]–[42] are for a long period or permanently in such states.

Obviously, in the mixed-mode region several relaxation LAO-s are always combined with only one SAO, and *vice versa* (Figs. 1, 2 and 3). Whereas the LAO-s are result of global phenomena, the SAO-s are determined by local conditions near the fold line of the critical manifold. Since we are here looking for tourbillion, the phenomenon that appears at the local level, we shall consider the cases with one LAO and several SAO-s as it is the case in Fig. 3 (a) and (b).
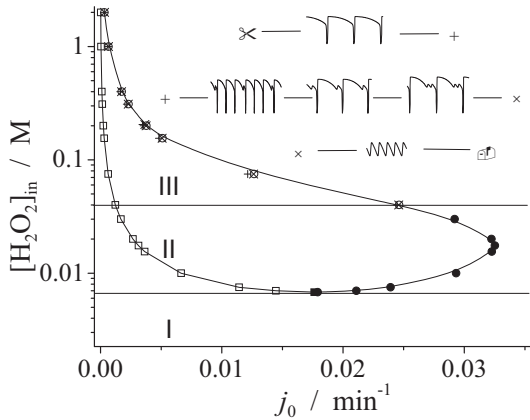
Figure 1. The dynamical states of the BL reaction as a function of two external parameters: the flow rate j_0 and hydrogen peroxide concentration in inflow $[H_2O_2]_{in}$. The oscillatory dynamical states are "inside" the curved line: there are no oscillations in region I for any j_0, there are only sustained relaxation oscillations in region II and all kind of oscillations including mixed-mode and chaotic ones in region III, depending on the j_0. The empty squares (□) denote the left supercritical Andronov-Hopf bifurcation points, the empty circles (○) denotes the right supercritical Andronov-Hopf bifurcation points, whereas the mixed-mode oscillations are between + and ×. The full square (■) at the left side of the last considered oscillatory state between regions I and II denotes subcritical Andronov-Hopf bifurcation point, whereas the full circles (●) on the right side denote the saddle loop bifurcation point. The typical periodic dynamical states in region III are presented at the right-upper corner.
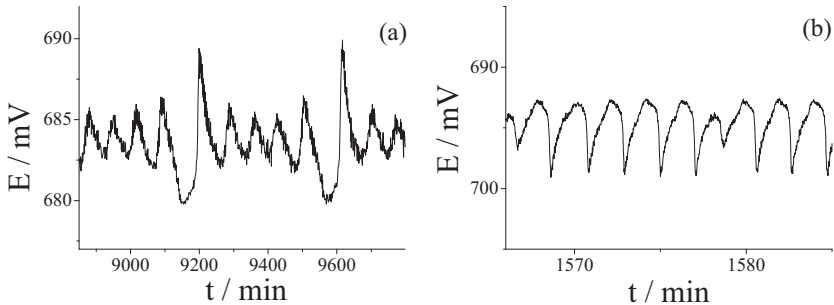

Figure 2. Experimental time series of the BL oscillatory reaction; $[KIO_3] = 0.059$ mol dm^{-3}, $[H_2O_2] = 0.15$ mol dm^{-3}; $j_0 = 0.0295$ min^{-1}, T = 56 °C. The inflow concentrations of sulfuric acid $[H_2SO_4]$ was (a) 0.0774 mol / dm^3 and (b) 0.0761 mol / dm^3.

In Fig. 3 we have presented separately slower and faster species. The slower species have higher concentrations than the faster ones. The iodine concentration is between the hydrogen peroxide and fast internal species ones, and, hence, it can be sometimes considered as the fast one. More precisely, iodine behaves as the fast variable when its concentration is in the stationary state, which is approximately satisfied in maxima and minima of the time-evolution concentration curve (Fig. 3). This phenomenon is easier to note in maxima where we can see numerous small oscillations in Fig 3 (a) and only one, or no one, in Fig. 3 (c). Moreover, comparing hydrogen peroxide with iodine time evolutions, we can see that iodine concentration is more likely in its global stationary state: the maxima of iodine concentrations do not depend on the position of an oscillation in a sequence during one period if there are lots of them.
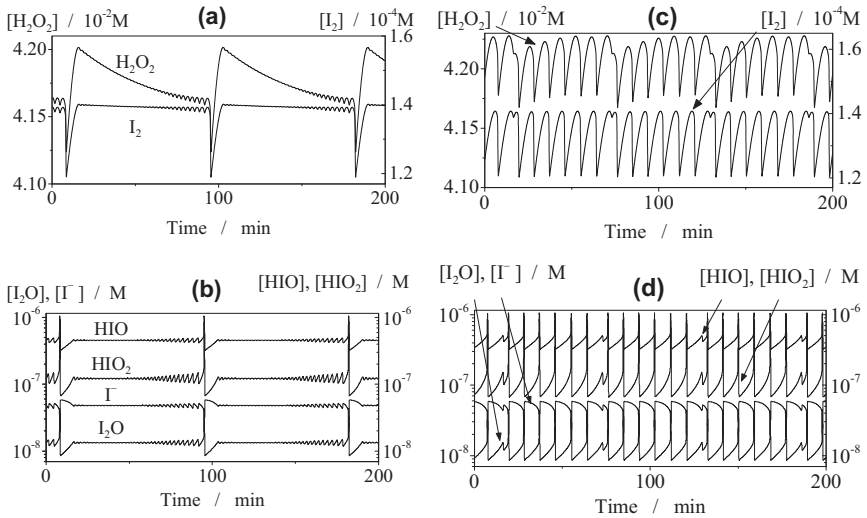
Figure 3. Mixed-mode oscillations of all internal species in BL reaction system for $[H_2O_2]_{in} = 0.155$ M and $j_0 = 5.0810 \times 10^{-3}$ min^{-1} for (a) and (b), and $j_0 = 4.82593 \times 10^{-3}$ min^{-1} for (c) and (d).

Described reaction dynamics characteristic for a system with multiple time scales in CSTR is strongly related to the dynamics of the corresponding system in batch reactor [71] and [72]. Both dynamical systems are organized by principally identical hypersurface in phase space. The main difference between them is caused by inflow of hydrogen peroxide that

exists only in CSTR. Hence, when the system is in the oscillatory state under batch conditions, the hydrogen peroxide decomposes monotonously but in stepwise form, while in CSTR the concentration of hydrogen peroxide, although constant in average, periodically decreases and increases in each SAO and in each LAO (Fig. 3 (a) and (c)). Analyzing Fig. 3 (a), we can see that hydrogen peroxide globally decreases during almost whole period, and after that increases just for a moment, to reach once more maximal value, whereas in the case given in Fig 3 (c), where several large-amplitude oscillations can be noted in one period, it globally increases until the last maximum before appearing a single small-amplitude oscillation. In other words, in one period obtained under CSTR conditions, depending on hydrogen peroxide inflow the concentration of hydrogen peroxide decreases and increases governing the whole system through phase space, over the trajectory described by the limit cycles as are the ones presented in Fig. 4.

Phase shifts between variables that can be noted in Fig. 4, is appropriate to study by means of two-dimensional projections of the phase space attractors. Species oscillating mainly in the same phase (Fig 4 a), have 2D attractors highly stretched out along the main diagonal. Phase shifts are connected with the order of reactions in reaction pathways generating oscillations.

Species oscillating mainly in the opposite phase (Fig 4 b) are also characterized by highly elongated phase portraits but transversally to the main diagonal. As we said before, in our case, the iodide concentration typically changes in the opposite phase with other fast species HIO, HIO_2 and I_2O, while they are almost synchronized among themselves and oscillate in the same phase. Slight banding of the phase portraits in Figs 4 (a) and 4 (b) is caused by slight phase shift among them. However, SAO-s are almost invisible at this graphic representation, since they are developed in a very thin slide of phase space along the LAO trajectory. Since fast species are so highly correlated, we can choose anyone of them to examine relations between slow and fast ones.

Phase portraits of couples with one slow and one fast species, (Fig 4 (c) and (d)) show distinct phase shift between species, since their limit cycles deviate significantly from the main diagonal and its transversal in both cases. However, there is a significant difference between two slow species. In the iodine phase portraits with fast species SAO-s are localized to relatively small neighborhood of the point where iodine concentration reaches its maximum value on the limit cycle. However, in hydrogen peroxide portraits with fast species, the SAO-s are stretched along wide range of hydrogen peroxide values.
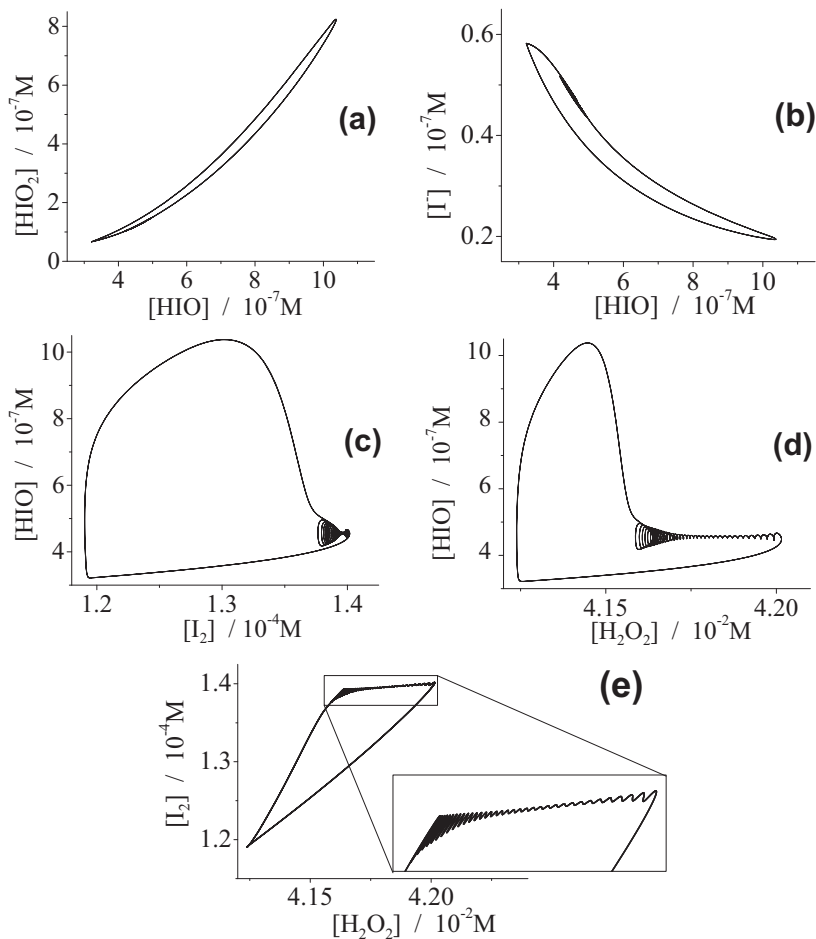
Figure 4. Phase portraits of the attractor for the BL reaction system simulation given in Fig. 3 (a) and (b). (a) HIO_2 *vs.* HIO, (b) I^- *vs.* HIO, (c) HIO *vs.* I_2, (d) HIO *vs.* H_2O_2, (e) I_2 *vs.* H_2O_2, with enlarged SAO-s in the inset part.

Moreover, in Figure 4 (e), the phase portrait of two slow species together with enlarged SAO-s in the inset part, is presented to illustrate distortion between two species in the insert, which are mainly in the same phase otherwise. Finally, the strong distortion of the limit cycle and apparent trajectory overlapping present in Fig. 4 (a)-(e) indicate that two-

dimensional projections of the limit cycle are not adequate representation for further analysis of the attractor, embedded in six dimensional phase space.

However, six-dimensional nonlinear dynamical system can be successfully considered (similarly many other multidimensional cases) as three-dimensional problem, since corresponding model consist of three-time scale types of variables: slow, fast and slow-fast. Therefore, three-dimensional projections of the phase space trajectory can be used to explore the mechanism of MMO-s in relation to the critical manifold of the slow-fast system.

4.2 Tourbillion

In Fig. 5 we can see the trajectory of the system from Fig. 3 (a) and (b) in three dimensional space including concentrations of three representative species with respect to their time-scale: hydrogen peroxide, iodine and HIO.
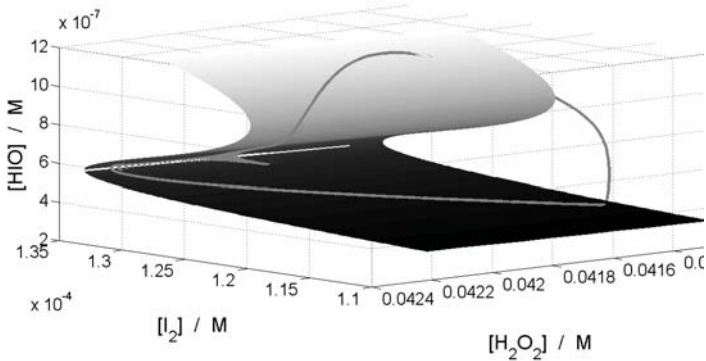
Figure 5. Part of the critical manifold for the BL model in CSTR, with attractor in the form of tourbillion. Parameters are as in Fig. 3 (a) and (b).

Generally, at all points along the fold line the determinant of the Jacobian matrix for fast species, passes through zero value – the matrix is singular [51]. This is also true for Jacobian matrix of four fast species in the model considered. Hence, the rank of the Jacobian is three on this line, and therefore, only three eigenvalues have non-zero values. The fourth value passes through zero on the fold line. It means that points on the fold line are of the saddle-node type with respect to the fast subsystem.

During an oscillatory period, dynamical system moves over one stable branch of critical manifold surface governed by its slow subsystem defined by H_2O_2 and iodine, until it

reaches the fold line, which is the solid line separating stable branch from the middle unstable one in Fig 5. At this point, we should expect the simple jump of the system to another stable branch of the surface. Instead this, in the transient state from the one to the other stable branch of the folded surface, the SAO-s of the canard form emerges. [1] This kind of the behavior is usually connected with some special point on the fold line: *folded singularity*.

At mentioned *folded singularity*, total differential of the rate equation for the fast species in slow (reduced) subsystem change its sign (equation (3)). Consequently, at such point, the trajectory of the slow subsystem over the stable branch of the manifold surface changes its direction, with respect to the fold line. More precisely, on one side of this point the trajectory of the slow subsystem is directed toward the fold line, and on the other side it goes away from the fold line. We used the equation (3) to locate the singularity on the fold line and found that it is placed at the intersection of the fold line with iodine nullcline (Figures 6 and 7). Then we evaluate eigenvalues of the slow subsystem at the singular point. It happens that both singular values in our case are real and negative, and hence, folded singularity should be of the folded node type.
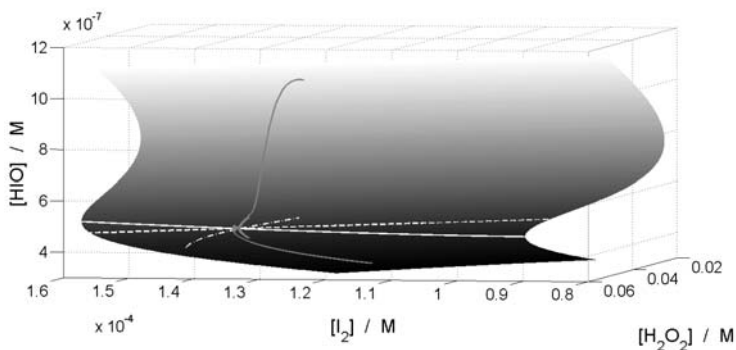
Figure 6 Part of the critical manifold for the BL model in CSTR, with indicated fold line (solid line) and two nullclines (dashed line for iodine and dash-dotted one for hydrogen peroxide). Parameters are as in Fig. 3 (a).

From Fig 6, we can see that the steady state of the full system (point at the crossing of two nullclines on the manifold surface – equilibrium) is near the fold line for parameter values used in this case, indicating possible *Singular Andronov-Hopf bifurcation*. It occurs when equilibrium of slow-fast system crosses the fold line. In the model considered, it could

be shown that for some higher values of the flow rate, equilibrium really crosses the fold line and goes to the other stable branch of the manifold becoming stable and suppressing any oscillations in the system. For mixed-mode oscillations to evolve from Singular Andronov-Hopf bifurcation mechanism, it would be expected that equilibrium be of the saddle-focus type, and SAO should increase in amplitude after they first come close to the equilibrium. However, equilibrium in our case is of the focus-node type. Moreover, SAO-s are in our case increasing while they are approaching to the equilibrium, not leaving from it.

Furthermore, singularities of the Andronov-Hopf type are not found for the subsystem which includes fast species only. However, five-dimensional (5D) fast subsystem including iodine species, too, really has the Andronov-Hopf point, on the corresponding iodine nullcline, in the near vicinity of the fold line. (Figure 7) We then evaluate the eigenvalues of the five-dimensional system along the iodine nullcline, and it happens that all but two are real and negative. Remaining two eigenvalues are complex conjugate, with changing sign of the real part in the Andronov-Hopf point. Due to the complex pair of eigenvalues in the 5D fast subsystem, trajectories spiral around the iodine nullcline, which gives rise to SAO-s. The amplitude of such an oscillation initially decreases (while system is moving along branch of the nullcline where the real part of the complex eigenvalues is negative) and then increases again (after the system goes beyond the Andronov-Hopf bifurcation and follows the part of the nullcline where real part becomes positive). This corresponds to a dynamical Andronov-Hopf bifurcation. [51] From this situation mixed-mode oscillations can occur by *delayed* Andronov-Hopf bifurcation or by the tourbillion mechanism. However, the difference among them is fuzzy and in practice they can be distinguished by subjective evaluation of the amplitude. [51] Namely, if the amplitude of the SAO-s is large enough that they are visible, then we have tourbillion and otherwise we have delayed Andronov-Hopf bifurcation. In the paper of Desroches *et al* there is distinguishing remark: "We adopt the term tourbillion from Wallet [68] to describe the trajectories passing through a Dynamical Andronov-Hopf bifurcation with oscillations whose amplitude remains above an observable threshold." In the case considered we could say that SAO-s are visible, and tourbillion is more probable variant.
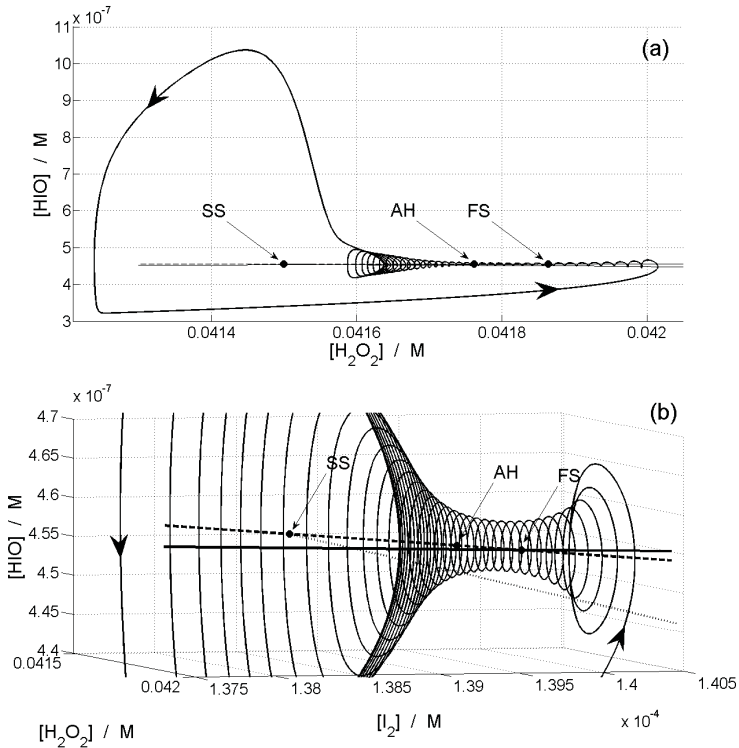
Figure 7. Folded singularity (FS) and Andronov-Hopf bifurcation point (AH) of the fast subsystem with iodine, found on the iodine nullcline (dashed line). Steady state (SS) of the full system is in the crossing of two nullclines. (a) Whole limit cycle in two dimensions. (b) Enlarged part in three dimensions with a fold line (solid line) and two nullclines (dashed and dotted lines). Parameters are as in Fig. 3 (a).

Iodine plays the most important role in this system being in a part fast, and otherwise slow variable. In the model discussed here, dynamical Andronov-Hopf bifurcation is present only in the five dimensional fast subsystem where iodine is included also. Therefore, the SAO-s emerging from dynamical Andronov-Hopf bifurcation, are developed only if the limit cycle of LAO-s, governed by folded singularity is close enough to iodine nullcline, so that iodine can behave like fast species.

5. Conclusion

Analyzing a model for the BL reaction in open reactor, with six independent intermediate species, with concentrations that differ for several orders of magnitudes, resulting therefore in multiple-time-scale evolution, we have found *tourbillion*.

The key detail for appearance of the tourbillion, the phenomenon that appear in the system with one slow and two fast variables at least, is the existence of slow-fast variable (iodine in the case considered) that change its property in mixed-mode oscillatory region transforming to fast species at the moment when system would jump from one to the other stable branch of the manifold. Thus a tourbillion occurs when considered BL reaction system having two slow and four fast variables, in the mixed-mode oscillatory region transforms for instant to the system with one slow and five fast variables.

The conclusion does not depend on the number of fast variables since all of them are interrelated and consequently they appear in the discussion as one.

The necessary condition to obtain tourbillion is that fast subsystem cross the Andronow-Hopf bifurcation near fold line. We demonstrate that appropriate Andronow-Hopf bifurcation occurs in slow-fast system, when one slow-fast variable transforms from the slow to the fast one near the fold. Critical role in the mechanism of the tourbillion shaped mixed-mode oscillations is the position of the Andronow-Hopf bifurcation, which ought to be located on the fast nullcline, between the steady state of the full system on one side and folded singularity on the other.

In the case of considered model of the BL reaction, the concentration of iodine species plays the role of slow-fast variable, changing its characteristics near the fold of the critical manifold. There, the Andronow-Hopf bifurcation occurs in the five dimensional fast subsystem, with appearance of two complex conjugate eigenvalues changing the sign of their real part. Lower dimensional fast subsystem posses no complex eigenvalues.

Hence, we come to the general statement that the tourbillion is a phenomenon that can emerge in the system with at least two slow and one fast variable when one slow variable changes to the fast one near the fold line.

Acknowledgement

Appendix

The time evolutions of intermediary species are described by the six following differential equations

$$d[H_2O_2]/dt = -r_5 - r_6 - r_8 + j_0 ([H_2O_2]_{in} - [H_2O_2])$$
$$d[I_2]/dt = r_{+4} - r_{-4} - j_0 [I_2]$$
$$d[I^-]/dt = -r_{+1} + r_{-1} - r_2 - r_{+4} + r_{-4} + r_5 - j_0 [I^-]$$
$$d[HIO]/dt = r_{+1} - r_{-1} + 2 r_{+3} - 2 r_{-3} - r_{+4} + r_{-4} - r_5 + r_6 - j_0 [HIO]$$
$$d[HIO_2]/dt = r_{+1} - r_{-1} - r_2 + r_6 + r_8 - j_0 [HIO_2]$$
$$d[I_2O]/dt = r_2 - r_{+3} + r_{-3} - r_6 - j_0 [I_2O].$$

Where rate expresions r_i are given in Table 1 of the main text. This system of ordinary differential equations defines our model of the BL reaction mechanism as a dynamical system.

We introduce new variables to make equations as shortest as possible:

$$a = [H_2O_2], \ b = [I_2], \ c = [I^-], \ d = [HIO], \ g = [HIO_2], \ f = [I_2O].$$

Now, symbolic calculation from steady state equations of four fast species gives following:

$g = -1/2 \ (k_6 \ k_7 \ a_2 \ j_o + 2 \ k_1 \ k_3 \ j_o + k_3 \ j_o^2 - 2 \ k_2 \ k_{-3} \ k_6 \ a \ d^2 - 3 \ k_2 \ k_3 \ k_8 \ a + 2 \ k_1 \ k_6 \ k_7 \ a^2 - 2 \ k_2 \ k_6 \ k_8 \ a^2$
$+ 2 \ k_2 \ k_{-3} \ d^2 \ j_o + 2 \ k_1 \ k_6 \ a \ j_o + k_2 \ d \ j_o^2 + k_{-1} \ d \ j_o^2 + k_7 \ a \ j_o^2 + k_6 \ a \ j_o^2 + 2 \ k_1 \ k_3 \ k_7 \ a + j_o^3 + 2 \ k_1 \ k_7 \ a \ j_o$
$+ k_2 \ k_3 \ d \ j_o + k_{-1} \ k_3 \ d \ j_o - k_2 \ k_8 \ a \ j_o + k_3 \ k_7 \ a \ j_o + k_{-1} \ k_6 \ a \ d \ j_o + 2 \ k_1 \ j_o^2 - (4 \ k_2 \ k_5 \ a \ d \ j_o^4 + 4 \ k_{-1} \ k_6 \ a \ d \ j_o^4$
$+ 4 \ k_2 \ k_{-3} \ k_6 \ a \ d^2 \ j_o^3 + 2 \ k_2 \ k_6 \ a \ d \ j_o^4 + 2 \ k_2 \ k_7 \ a \ d \ j_o^4 + 16 \ k_1 \ k_2 \ k_6 \ k_7 \ a^2 \ d \ j_o^2 + 4 \ k_2^2 \ k_{-3} \ d^3 \ j_o^3 + 4 \ k_1 \ k_6^2 \ a^2 \ j_o^3 + 4$
$k_1 \ k_3^2 \ k_7^2 \ a^2 \ j_o + 4 \ k_2 \ k_3^2 \ k_5 \ k_7 \ a^2 \ d \ j_o + 8 \ k_2 \ k_3 \ k_{-3} \ k_6 \ k_7 \ a^2 \ d^2 \ j_o + k_7^2 \ a^2 \ j_o^4 + k_{-1}^2 \ d^2 \ j_o^4 + 4 \ k_1^2 \ k_3^2 \ j_o^2$
$+ k_6^2 \ a^2 \ j_o^4 + k_2^2 \ d^2 \ j_o^4 + 2 \ k_7 \ a \ j_o^5 + 2 \ k_{-1} \ d \ j_o^5 + 2 \ k_6 \ a \ j_o^5 + 2 \ k_2 \ d \ j_o^5 + 8 \ k_1^2 \ k_3 \ j_o^3 + 4 \ k_1 \ k_3^2 \ j_o^3 + 8 \ k_1 \ k_3 \ j_o^4$
$+ 6 \ k_2 \ k_3^2 \ k_8 \ a \ j_o^2 + 4 \ k_2 \ k_3 \ k_{-3} \ d^2 \ j_o^3 + 10 \ k_2 \ k_3 \ k_6 \ k_8 \ a^2 \ j_o^2 + 8 \ k_2 \ k_3 \ k_5 \ a \ d \ j_o^3 + 8 \ k_1 \ k_3 \ k_6 \ a \ j_o^3$
$+ 4 \ k_{-1} \ k_3 \ k_6 \ a \ d \ j_o^3 + 8 \ k_1 \ k_3^2 \ k_7 \ a \ j_o^2 + 16 \ k_1 \ k_3 \ k_7 \ a \ j_o^3 + 4 \ k_2 \ k_3^2 \ k_5 \ a \ d \ j_o^2 + 8 \ k_2 \ k_3 \ k_{-3} \ k_6 \ a \ d^2 \ j_o^2$
$+ 24 \ k_1 k_2 \ k_3 \ d \ j_o^3 + 2 \ k_2 \ k_3 \ k_6 \ a \ d \ j_o^4 + 16 \ k_1 \ k_2 \ k_3^2 \ d \ j_o^2 + 4 \ k_{-1} \ k_2 \ k_3 \ d^2 \ j_o^3 + 4 \ k_2 \ k_3 \ k_7 \ a \ d \ j_o^3$
$- 6 \ k_2^2 \ k_3^2 \ k_8 \ a \ d \ j_o + 24 \ k_1 \ k_2 \ k_5 \ k_6 \ k_7 \ a^2 \ d^2 \ j_o + 4 \ k_1^2 \ j_o^4 + 8 \ k_1 \ k_{-1} \ k_2 \ k_3^2 \ k_6 \ a^2 \ d^2 \ j_o + 16 \ k_1 \ k_2 \ k_5 \ k_6^2 \ k_7 \ a^4 \ d$
$+ 8 \ k_1 \ k_2 \ k_6^2 \ k_7 \ a^3 \ d \ j_o + 8 \ k_1^2 \ k_3 \ k_7^2 \ a^2 \ j_o + 32 \ k_1 \ k_2 \ k_3^2 \ k_5 \ k_7 \ a^2 \ d + 28 \ k_1 \ k_2 \ k_3 \ k_{-3} \ k_6 \ k_7 \ a^2 \ d^2$
$+ 4 \ k_1 \ k_{-1} \ k_6^2 \ a^2 \ d \ j_o^2 + 48 \ k_1 \ k_2 \ k_3 \ k_5 \ k_6 \ a^2 \ d \ j_o + 16 \ k_1 \ k_{-3} \ k_6^2 \ a^2 \ d^2 \ j_o + 60 \ k_1 \ k_{-1} \ k_2 \ k_3 \ k_{-3} \ k_6 \ a \ d^3$
$+ 20 \ k_1 \ k_{-1} \ k_2 \ k_3^2 \ d^2 \ j_o + 40 \ k_1 \ k_{-1} \ k_2 \ k_3 \ k_{-3} \ d^3 \ j_o + 56 \ k_1 \ k_{-1} \ k_2 \ k_3 \ k_6 \ k_8 \ a^2 \ d + 40 \ k_1 \ k_{-1} \ k_2 \ k_3^2 \ k_8 \ a \ d$
$+ 64 \ k_1 \ k_{-1} \ k_2 \ k_5 \ k_8 \ a \ d \ j_o + 56 \ k_1 \ k_{-1} \ k_2 \ k_3 \ k_5 \ k_6 \ a^2 \ d^2 + 40 \ k_1 \ k_{-1} \ k_2 \ k_3^2 \ k_5 \ a \ d^2 + 32 \ k_1 \ k_{-1} \ k_2 \ k_3 \ d^2 \ j_o^2$
$+ 8 \ k_1 \ k_{-1} \ k_3 \ k_6 \ k_7 \ a^2 \ d \ j_o + 28 \ k_1 \ k_2 \ k_{-3} \ k_6 \ k_7 \ a^2 \ d^2 \ j_o + 8 \ k_1 \ k_2 \ k_6^2 \ k_7 \ k_8 \ a^4 + 32 \ k_1 \ k_2 \ k_5 \ k_6 \ k_7 \ a^3 \ d \ j_o$
$+ 8 \ k_1^2 \ k_6^2 \ k_7 \ a^3 \ j_o + 4 \ k_1 \ k_{-1} \ k_6^2 \ k_7 \ a^3 \ d \ j_o + 8 \ k_1^2 \ k_3 \ k_6 \ k_7^2 \ a^3 + 8 \ k_1^2 \ k_6 \ k_7^2 \ a^3 \ j_o + 48 \ k_1 \ k_2 \ k_3 \ k_5 \ k_6 \ k_7 \ a^3 \ d$
$+ 16 \ k_1 \ k_2 \ k_{-3} \ k_6^2 \ k_7 \ a^3 \ d^2 + 2 \ k_{-1}^2 \ k_7 \ a \ d \ j_o^4 + 8 \ k_1 \ k_{-1} \ k_6 \ k_7 \ a^2 \ d \ j_o^2 + 4 \ k_{-1} \ k_2 \ k_{-3} \ d^3 \ j_o^3 + 4 \ k_{-1} \ k_2 \ k_5 \ a \ d^2 \ j_o^3$
$+ 2 \ k_{-1}^2 \ k_6 \ a \ d^2 \ j_o^3 + 4 \ k_{-1} \ k_3 \ k_7 \ a \ d \ j_o^3 + 8 \ k_1 \ k_{-1} \ k_3 \ k_7 \ a \ d \ j_o^2 + 4 \ k_1 \ k_{-1} \ k_7 \ a \ d \ j_o^3 + 8 \ k_{-1} \ k_2 \ k_3 \ k_5 \ a \ d^2 \ j_o^2$
$+ 12 \ k_{-1} \ k_2 \ k_{-3} \ k_6 \ a \ d^3 \ j_o^2 + k_{-1}^2 \ k_6^2 \ a^2 \ d^2 \ j_o^2 + 4 \ k_{-1} \ k_2 \ k_3 \ k_5 \ k_6 \ a^2 \ d^2 \ j_o + 4 \ k_{-1} \ k_2 \ k_6^2 \ a^2 \ d^3 \ j_o$
$+ 8 \ k_1^2 \ k_3^2 \ k_7 \ a \ j_o + 32 \ k_1 \ k^2 \ k_3^2 \ k_5 \ a \ d \ j_o + 28 \ k_1 \ k_2 \ k_3 \ k_{-3} \ k_6 \ a \ d^2 \ j_o + 2 \ k_{-1}^2 \ k_3 \ d^2 \ j_o^2 + 2 \ k_3 \ k_7^2 \ a^2 \ j_o^3$
$+ 4 \ k_1 \ k_7^2 \ a^2 \ j_o^3 + 9 \ k_2^2 \ k_3^2 \ k_8^2 \ a^2 + 4 \ k_1^2 \ k_6^2 \ k_7^2 \ a^4 + k_{-1}^2 \ k_3^2 \ d^2 \ j_o^2 + 4 \ k_{-1} \ k_3 \ d \ j_o^4 + 4 \ k_3 \ k_7 \ a \ j_o^4$
$+ 2 \ k_{-1} \ k_3^2 \ d \ j_o^3 + 2 \ k_3^2 \ k_7 \ a \ j_o^3 + k_2^2 \ k_3^2 \ d^2 \ j_o^2 + 2 \ k_2^2 \ k_3 d^2 \ j_o^3 + 8 \ k_1 \ k_2 \ d \ j_o^4 + 8 \ k_1 \ k_6 \ a \ j_o^4 + 4 \ k_1 \ k_{-1} \ d \ j_o^4$
$+ 8 \ k_1 \ k_7 \ a \ j_o^4 + 8 \ k_1^2 \ k_6 \ a \ j_o^3 + 8 \ k_1^2 \ k_7 \ a \ j_o^3 + 4 \ k_2 \ k_{-3} \ d^2 \ j_o^4 + 2 \ k_3^2 \ d^2 \ j_o^4 + 2 \ k_{-1} \ k_2 \ d^2 \ j_o^2$
$+ 4 \ k_2^2 \ k_3 \ k_{-3} \ d^3 \ j_o^2 - 4 \ k_2^2 \ k_3 \ k_6 \ k_8 \ a^2 \ d \ j_o + 8 \ k_2^2 \ k_3 \ k_5 \ a \ d^2 \ j_o^2 + 24 \ k_1 \ k_2 \ k_3 \ k_6 \ a \ d \ j_o^2 + 2 \ k_{-1} \ k_2 \ k_3 \ k_6 \ a \ d^2 \ j_o^2 + 2 \ k_2$
$k_3^2 \ k_7 \ a \ d \ j_o^2 + 16 \ k_1 \ k_2 \ k_3^2 \ k_7 \ a \ d \ j_o + 24 \ k_1 \ k_2 \ k_3 \ k_7 \ a \ d \ j_o^2 + 4 \ k_2^2 \ k_3^2 \ k_5 \ a \ d^2 \ j_o - 4 \ k_2^2 \ k_3 \ k_{-3} \ k_6 \ a \ d^3 \ j_o + 16 \ k_1^2 \ k_6$
$k_7 \ a^2 \ j_o^2 + 8 \ k_1 \ k_{-1} \ k_3 \ d \ j_o^3 + 16 \ k_1 \ k_2 \ k_{-3} \ d^3 \ j_o^3 + j_o^6 + 2 \ k_2 \ k_3 \ k_6 \ k_7 \ a^2 \ d \ j_o^2 + 16 \ k_1 \ k_6 \ k_7 \ a^2 \ j_o^3$
$+ 2 \ k_2 \ k_6 \ k_7 \ a^2 \ d \ j_o^3 + 16 \ k_1 \ k_3 \ k_6 \ k_7 \ a^2 \ j_o^2 + 4 \ k_{-1} \ k_6 \ k_7 \ a^2 \ d \ j_o^3 + 10 \ k_2 \ k_3 \ k_6 \ k_7 \ k_8 \ a^3 \ j_o + 4 \ k_1 \ k_6^2 \ k_7^2 \ a^4 \ j_o$
$+ 4 \ k_{-1} \ k_3 \ k_6 \ k_7 \ a^2 \ d^2 \ j_o^2 + 4 \ k_2 \ k_{-3} \ k_6 \ k_7 \ a^2 \ d^2 \ j_o^2 + 4 \ k_2 \ k_6^2 \ k_7 \ a^3 \ d \ j_o + 4 \ k_2 \ k_3 \ k_6 \ k_7 \ a^3 \ j_o^2 + 8 \ k_1 \ k_6^2 \ k_7 \ a^3 \ j_o^2 + 2 \ k_{-}$
$_1 \ k_6^2 \ k_7 \ a^3 \ d \ j_o^2 + 2 \ k_3 \ k_6 \ k_7^2 \ a^3 \ j_o^2 + 8 \ k_1 \ k_3 \ k_6 \ k_7^2 \ a^3 \ j_o + 8 \ k_1 \ k_6 \ k_7^2 \ a^3 \ j_o^2 + 4 \ k_2 \ k_3 \ k_5 \ k_6 \ k_7 \ a^3 \ d \ j_o$
$+ 4 \ k_2 \ k_{-3} \ k_6^2 \ k_7 \ a^3 \ d^2 \ j_o + k_3^2 \ j_o^4 + 2 \ k_3 \ j_o^5 + 4 \ k_{-1} \ j_o^5 + k_3^2 \ k_7^2 \ a^2 \ j_o^2 + 4 \ k_1^2 \ k_3^2 \ k_7^2 \ a^2 + 4 \ k_1^2 \ k_7^2 \ a^2 \ j_o^2$
$+ 16 \ k_1 \ k_2 \ k_5 \ a \ d \ j_o^3 + 8 \ k_1 \ k_{-1} \ k_6 \ a \ d \ j_o^3 + 16 \ k_1^2 \ k_3 \ k_7 \ a \ j_o^2 + 48 \ k_1 \ k_2 \ k_3 \ k_5 \ a \ d \ j_o^2 + 28 \ k_1 \ k_2 \ k_{-3} \ k_6 \ a \ d^2 \ j_o^2$
$+ 28 \ k_1 \ k_{-1} \ k_2 \ k_3 \ k_6 \ a \ d^2 \ j_o + 64 \ k_1 \ k_{-1} \ k_2 \ k_5 \ a \ d^2 \ j_o - 8 \ k_2^2 \ k_5 \ k_6 \ k_8 \ a^3 \ d \ j_o + 8 \ k_1 \ k_2 \ k_6^2 \ k_8 \ a^3 \ j_o$
$+ 4 \ k_{-1} \ k_2 \ k_6^2 \ k_8 \ a^3 \ d \ j_o - 8 \ k_2^2 \ k_3 \ k_5 \ k_6 \ k_8 \ a^3 \ d + 8 \ k_2^2 \ k_{-3} \ k_6^2 \ a^3 \ d^2 + 4 \ k_2^2 \ k_3^2 \ k_5^2 \ a^2 \ d^2 + 8 \ k_2 \ k_3 \ k_8 \ a \ j_o^3$
$- 8 \ k_2^2 \ k_3 \ k_8 \ a \ d \ j_o^2 + 4 \ k_1 \ k_2 \ k_8 \ a \ j_o^3 + 2 \ k_2 \ k_8 \ a \ j_o^4 + k_6^2 \ k_7^2 \ a^4 \ j_o^2 + 4 \ k_6 \ k_7 \ a_2^2 j_o^4 + 2 \ k_6^2 \ k_7 \ a^3 \ j_o^3$

$+ 2 k_6 k_7^2 a^3 j_o^3 + 2 k_2 k_3^2 j_o^3 d + 4 k_2 k_3 j_o^4 d + 2 k_3 k_6 a j_o^4 - 2 k_2^2 k_8 a d j_o^3 + 4 k_{-1} k_2 k_3 k_{-3} d^3 j_o^2$

$+ 2 k_{-1}^2 k_3 k_6 a d^2 j_o^2 + 2 k_{-1} k_3^2 k_7 a d j_o^2 + 4 k_1 k_{-1} k_3^2 k_7 a d j_o + 4 k_{-1} k_2 k_3^2 k_5 a d^2 j_o$

$+ 16 k_{-1} k_2 k_3 k_{-3} k_6 a d^3 j_o + 4 k_2^2 k_{-3}^2 d^4 j_o^2 + 4 k_2 k_{-3} k_7 a d^2 j_o^3 + 4 k_2 k_5 k_7 a^2 d j_o^3 + 8 k_1 k_3 k_7^2 a^2 j_o^2$

$+ 8 k_2 k_3 k_5 k_7 a^2 d j_o^2 + 16 k_1 k_2 k_5 k_6^2 a^3 d j_o + 8 k_1 k_2 k_6^2 a^2 d^2 j_o^2 + 12 k_1 k_{-1} k_2 d^2 j_o^3$

$+ 52 k_1 k_{-1} k_2 k_{-3} k_6 a d^3 j_o + 24 k_1 k_{-1} k_2 k_{-3} d^3 j_o^2 + 40 k_1 k_{-1} k_2 k_6 k_8 a^2 d^2 j_o + 24 k_1 k_{-1} k_2 k_8 a d j_o^2$

$+ 40 k_1 k_{-1} k_2 k_5 k_6 a^2 d^2 j_o + 20 k_1 k_{-1} k_2 k_6 a d^2 j_o^2 + 24 k_1 k_{-1} k_2 k_5 a^2 d^2 j_o^2 + 4 k_2^2 k_5^2 a^2 d^2 j_o^2$

$+ 32 k_1 k_2 k_5 k_6 a^2 d j_o^2 + 4 k_{-1} k_2 k_5 k_6 a^2 d^2 j_o^2 + 48 k_1 k_2 k_3 k_5 k_7 a^2 d j_o + 16 k_1 k_2 k_5 k_7 a^2 d j_o^2$

$+ 8 k_2^2 k_3 k_5^2 a^2 d^2 j_o - 8 k_2^2 k_{-3} k_5 k_6 a^2 d^3 j_o + 4 k_1^2 k_6^2 a^2 j_o^2 + 4 k_2^2 k_{-3}^2 k_6^2 a^2 d^4 - 4 k_2^2 k_6 k_8 a^2 d j_o^2$

$+ 4 k_2 k_5 a d^2 j_o^3 + 16 k_1 k_2 k_6 a d j_o^3 + 2 k_{-1} k_2 k_6 a d^2 j_o^3 + 8 k_1 k_2 k_7 a d j_o^3 - 4 k_2^2 k_{-3} k_6 a d^3 j_o^2$

$+ 4 k_2 k_6^2 k_8 a^3 j_o^2 + 4 k_2 k_5 k_6 a^2 d j_o^3 + 2 k_{-1} k_2 k_6^2 a^2 d j_o^3 + 4 k_2 k_3 k_5 k_6 a^2 d^2 j_o^2 + 4 k_2 k_{-3} k_6^2 a^2 d^2 j_o^2$

$+ 12 k_1 k_2 k_3^2 k_8 a j_o + 16 k_1^2 k_3 k_6 k_7 a^2 j_o + 4 k_1 k_{-1} k_3^2 d j_o^2 + 32 k_1 k_2 k_3 k_{-3} d^2 j_o^2 + 20 k_1 k_2 k_3 k_6 k_8 a^2 j_o$

$+ 8 k_1^2 k_3 k_6 a j_o^2 + 8 k_1 k_{-1} k_3 k_6 a d j_o^2 + 6 k_2 k_6 k_7 k_8 a^3 j_o^2 - 8 k_2^2 k_3 k_{-3} k_5 k_6 a^2 d^3 + 8 k_2^2 k_3 k_{-3} k_5 a d^3 j_o$

$- 8 k_2^2 k_{-3}^2 k_6 a d^4 j_o + 4 k_2^2 k_6^2 k_8^2 a^4 + k_2^2 k_8^2 a^2 j_o^2 + 8 k_2^2 k_{-3} k_5 a d^3 j_o^2 + 4 k_2 k_{-3} k_7 a d^2 j_o^2$

$+ 32 k_1 k_2 k_3 k_{-3} k_7 a d^2 j_o + 16 k_1 k_2 k_{-3} k_7 a d^2 j_o^2 + 24 k_1 k_{-1} k_2 k_{-3} k_6^2 a^2 d^3 + 16 k_1 k_{-1} k_2 k_6^2 k_8 a^3 d$

$+ 16 k_1 k_{-1} k_2 k_5 k_6^2 a^3 d^2 + 6 k_2 k_6 k_8 a^2 j_o^3 + 16 k_1 k_2 k_3 k_8 a j_o^2 + 10 k_{-1} k_2 k_8 a d j_o^3 + 2 k_2 k_7 k_8 a^2 j_o^3$

$+ 6 k_2^2 k_3 k_8^2 a^2 j_o + 12 k_1 k_2 k_6 k_7 k_8 a^3 j_o + 24 k_{-1} k_2 k_3 k_8 a d j_o^2 - 4 k_2^2 k_{-3} k_8 a d^2 j_o^2 + 4 k_2^2 k_6 k_8^2 a^3 j_o$

$- 4 k_2^2 k_5 k_8 a^2 d j_o^2 + 12 k_1 k_2 k_6 k_8 a^2 j_o^2 + 14 k_{-1} k_2 k_6 k_8 a^2 d j_o^2 + 8 k_2 k_3 k_7 k_8 a^2 j_o^2$

$+ 16 k_1 k_2 k_3 k_7 k_8 a^2 j_o + 4 k_1 k_2 k_7 k_8 a^2 j_o^2 - 16 k_2^2 k_3 k_5 k_8 a^2 d j_o - 4 k_2^2 k_{-3} k_6 k_8 a^2 d^2 j_o + 4 k_3 k_6 k_7 a^2 j_o^3$

$+ 20 k_1 k_2 k_3 k_6 k_7 k_8 a^3 + 14 k_{-1} k_2 k_3^2 k_8 a d j_o - 12 k_2^2 k_{-3} k_3 k_8 a d^2 j_o + 12 k_2^2 k_3 k_6 k_8^2 a^3$

$+ 18 k_{-1} k_2 k_3 k_6 k_8 a^2 d j_o + 6 k_2 k_3^2 k_7 k_8 a^2 j_o + 12 k_1 k_2 k_3^2 k_7 k_8 a^2 - 12 k_2^2 k_3^2 k_5 k_8 a^2 d$

$+ 12 k_2^2 k_3 k_{-3} k_6 k_8 a^2 d^2)^{1/2} + 2 k_2 k_3 k_5 a d + 2 k_2 k_5 a d j_o) / (k_2 (5 k_{-1} k_3 d + 3 k_3 j_o + a k_7 j_o + 2 k_6 a j_o$

$+ 3 k_{-1} d j_o + j_o^2 + 3 k_3 k_7 a + 2 k_{-1} k_6 a d + 2 k_6 k_7 a^2))$;

$c = d (2 k_1 k_3 g + 2 k_{-1} k_6 a g + 2 k_{-1} g j_o + 2 k_3 k_5 a + 2 k_5 k_6 a^2 + 2 k_5 a j_o + k_{-3} k_6 a d + 2 k_{-3} d j_o + k_3 j_o + k_6 a$

$j_o + j_o^2) / (2 k_1 k_3 + 2 k_1 k_6 a + 2 k_1 j_o + 3 k_2 k_3 g + 2 k_2 k_6 a g + k_2 g j_o + k_3 j_o + k_6 a j_o + j_o^2)$;

$f = (k_2 c g + k_{-3} d^2) / (k_3 + k_6 a + j_o)$;

$b = (- k_1 c + k_{-1} d g - 2 k_3 f + 2 k_{-3} d^2 + k_4 c d + k_5 a d - k_6 a f + d j_o) / k_{-4}$;

Hence, variables b, c, g and f are given as a functions of variables a and d, only.

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