Special Positive Systems: the QP and the Reaction Kinetic System Class

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Abstract The class of reaction kinetic systems as a special sub-class of positive systems is investigated in this paper. The original notion based on the kinetical equations obeying mass action law has been generalized to cover the cases with real exponents in the reaction monomials. It has been shown that the generalized class still possesses the same stability property under the usual Lyapunov function. Thereafter the relationship between the reaction kinetic and the quasi-polynomial (QP) systems classes is established based on their algebraic characterization, and a method is proposed to test if a QP system has a generalized reaction kinetic realization. Simple algebraic conditions are also given for general Lotka-Volterra systems that guarantee the existence of theeir reaction kinetic model form.

1 Introduction

Positive systems form an important class of nonlinear systems [4, 3] where the state variables are positive (i.e. the positive orthant denoted by $\mathbb{R}^n_+$ is invariant for the dynamics). In some application areas, such as process systems or transportation systems the underlying physics and chemistry ensures and at the same times requires that the variables (such as masses and component masses in a holdup, temperatures, pressures and alike) are positive.

Reaction kinetic systems form a special class of positive systems with smooth nonlinearities where advantageous dynamic properties, such as global asymptotic stability may be ensured thanks to the special structure of the system model. In the

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classical case, these systems are descibed by a set of ordinary differential equations (ODEs) with polynomial right-hand sides. The dynamical properties of reaction kinetic systems have been investigated by many authors, mainly the number and local stability of steady state solutions and conditions for global stability (see, e.g. [6], [5], [2], [16] and [8]) have been dealt with.

There is another, related class of special nonlinear systems, the class of quasi-polynomial (QP) or generalized Lotka-Volterra (GLV) systems (see e.g. [12], [10]), that are generalizations of the classical Lotka-Volterra system model described by a set of ODEs with second-order polynomial right-hand sides. QP systems have a special algebraic structure and a simple Lyapunov function candidate [7], [9] that enables the test of global asymptotic stability by using LMIs. It is very easy to see that reaction kinetic systems are special sub-classes of QP systems, but the exact relationship and its consequences are not characterized well enough.

Despite of the above mentioned results, not much have been done, however, to use the above special strong results in the area of nonlinear systems and control theory. As a first step, the ideas on description and stability of reaction kinetic systems were recalled, extended and put into a control theoretic framework in [16].

The aim of this paper is to investigate the relationship between the reaction kinetic and QP systems classes in order to generalize the reaction kinetic class in such a way that the generalized class preserves the advantageous properties and extends its descriptive power.

2 The reaction kinetic system class

The original physical picture underlying the reaction kinetic system class is a closed system under isothermal and isobaric conditions, where chemical species $\mathbf{X}_i$, $i = 1, ..., n$ take part in r chemical reactions. The systems is perfectly stirred, i.e. concentrated parameter in the simplest case. The concentrations x_i, $i = 1, ..., n$ form the state vector the elements of which are positive by nature.

For the sake of simplicity, physico-chemical properties and the total mass (volume) of the system are assumed to be constant.

2.1 Reaction systems obeying the mass action law (MAL)

The origin of mass action law lies in the *molecular collision picture* of chemical reactions. Here the reaction occurs when either two reactant molecules collide, or a reactant molecule collides with an inactive (e.g. solvent) molecule. Clearly, the probability of having a reaction is proportional to the probability of collisions, that is proportional to the concentration of the reactant(s). It is important to note that the probability of having a three molecular collision is negligible compared to the two molecular collisions, therefore at most second order reaction kinetic models are

fully compatible with the molecular collision picture. It is also emphasized however, that many important dynamic properties of reaction systems as a system class do not depend on their order.

2.1.1 Irreversible reactions obeying the mass action law

A straightforward generalization of the above molecular collision picture is when we allow to have multi-molecule collisions to have *elementary reaction steps* in the following form:

$$\sum_{i=1}^{n} \alpha_{ij}\mathbf{X}_i \rightarrow \sum_{i=1}^{n} \beta_{ij}\mathbf{X}_i \quad j = 1,...,r' \tag{1}$$
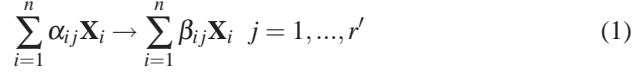
where α_{ij} is the so-called *stoichiometric coefficient* of component $\mathbf{X}_i$ in the jth reaction, i.e. the number of colliding $\mathbf{X}_i$ molecules, and $\beta_{i\ell}$ is the stoichiometric coefficient of the product $\mathbf{X}_\ell$. Note that *the stoichiometric coefficients are always non-negative integers in classical reaction kinetic systems*.

According to the extended molecular picture, the reaction rate of the above reactions can be described as

$$\rho_j = k_j \prod_{i=1}^{n} [\mathbf{X}_i]^{\alpha_{ij}} = k_j \prod_{i=1}^{n} x_i^{\alpha_{ij}} \quad , \quad j = 1,...,r' \tag{2}$$

where $[\mathbf{X}_i] = x_i$ is the concentration of the component $\mathbf{X}_i$, and $k_j > 0$ is the *reaction rate constant* of the jth reaction, that is always positive.

2.1.2 Reversible reactions obeying the mass action law

A special class of reaction kinetic systems is the case of reversible reactions the rate equations of which obey the mass action law (MAL) (see [5]).

The reaction scheme consists of r reversible reactions of the form

$$\sum_{i=1}^{n} \alpha_{ij}\mathbf{X}_i \rightleftarrows \sum_{i=1}^{n} \beta_{ij}\mathbf{X}_i \quad j = 1,...,r \tag{3}$$
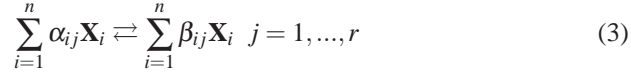
The set of components with non-zero stoichiometric coefficients α_{ij} or β_{ij} on a side of a reaction form a so called complex C_k. Therefore we have $2r$ complexes from which there can be identical complexes, i.e. $k = 1,...,m$, $m \leq 2r$. Note that the reversible equations (3) can be realized as $r' = 2r$ irreversible reaction steps (1).

The mass action law type reaction rates can also be applied to this reversible case by considering the rate of the jth reversible step in the form:

$$W_j(x) = W_j^+(x) - W_j^-(x) = k_j^+ \prod_{i=1}^{n} x_i^{\alpha_{ij}} - k_j^- \prod_{x=1}^{n} x_i^{\beta_{ij}} \tag{4}$$

with x_i being the concentration of the component $\mathbf{X}_i$. Here both *reaction rate constants* $k_j^+ > 0$ and $k_j^- > 0$ are strictly positive. The terms $W_j^+(x)$ and $W_j^-(x)$ are the reaction rates of the forward and backward directed reaction steps, respectively.

2.1.3 Generalized reaction kinetic systems with MAL kinetics

One can generalize the above reaction kinetic system models with MAL kinetics in both the reversible and irreversible cases, if *real stoichiometric coefficients* are allowed. This means that *the stoichiometric coefficients α_{ij} or β_{ij} can have real values, but the reaction rate constants remain strictly positive*.

It can be shown that both the realization properties (see later in section 3) and the stability properties will remain the same if the internal relationships between the algebraic realization matrices (see in subsection 2.2) hold.

2.2 Algebraic characterization

The parameters of the above introduced reaction kinetic system class and their structural relationships are investigated here to find properties that ensure that a set of ordinary differential equations with polynomial right-hand side enables a reaction kinetic system interpretation.

2.2.1 The Gorban description

The case when the reaction kinetic system consists of only reversible reactions that obey the mass action law was first investigated by Gorban [2], therefore we shall call the description of this case *Gorban description*.

The reaction rate equations originate from the component mass balances, and they are in the form

$$\frac{dx}{dt} = \mathcal{N}W(x) \tag{5}$$

where $x \in \mathbb{R}^n$ is the state vector are constructed from the concentrations of the components (species). $\mathcal{N} \in \mathbb{R}^{n \times r}$ is the stoichiometric matrix, and $W \in \mathbb{R}^r$ is the reaction rate vector described in Eq. (4).

The *stoichiometric matrix $\mathcal{N}$* is constructed form the stoichiometric coefficients α_{ij} and β_{ij} in the following way. To each complex C_k a column vector $v^{(k)} \in \mathbb{R}^n$ is associated such that $v_i^{(k)} = \alpha_{ik}$, in other words $v_i^{(k)} = \alpha_{ik}$ stores the stoichiometric coefficient of the component $\mathbf{X}_i$ in the complex. Note that precisely two complexes take part in a reaction (see Eq. (3)) thus one can form two matrices $\mathcal{N}^{(\alpha)}$ from the complexes of the left hand sides of the r reactions, and $\mathcal{N}^{(\beta)}$ from that of the right hand sides by collecting the column vectors $v^{(k)}$ of the corresponding complexes. Thus $\mathcal{N}$ is simply the difference of the two, i.e. $\mathcal{N} = \mathcal{N}^{(\beta)} - \mathcal{N}^{(\alpha)}$ where the

jth column vector of $\mathcal{N}$, $\mu^{(j)} \in \mathbb{R}^n$ contains the difference of the stoichiometric coefficients of the jth reaction.

Note that the parameters that describe a reaction kinetic system with reversible MAL kinetics in its Gorban form are given by the stoichiometric matrix $\mathcal{N}$ and the reaction rate coefficients $k^+ = [k_1^+...k_r^+]^T$ and $k^- = [k_1^-...k_r^-]^T$. However, one cannot uniquely determine the stoichiometric coefficients from the stoichiometric matrix $\mathcal{N}$ when $\alpha_{ij} \cdot \beta_{ij} \neq 0$, i.e. when a component is present on both the righ and the left hand side of a reaction. Unfortunately, an important reaction type, the so called *catalytic reactions* belong to this category.

2.2.2 The Feinberg description

Another way of representing a reaction kinetic system with MAL kinetics is *to relax the assumption of reversible reaction steps and consider each irreversible steps individually*. We shall name this description the Feinberg description after Feinberg [5], who first investigated this case. Then the reaction rates are described using the so-called *reaction monomials* associated to the complexes in the form

$$\varphi_j(x) = \prod_{i=1}^{n} x_i^{y_{ij}} \tag{6}$$

where the elements of the matrix Y are the stoichiometric coefficients of the components i, $i = 1,...,n$ in the complexes j, $j = 1,...,m$

$$[Y]_{ij} = y_{ij}$$

Note that the stoichiometric coefficients α_{ij} of the reactants in the irreversible reaction steps (1) appear in the matrix Y, while the reaction monomials are the principal factors in the MAL reaction rate expression (2). In the general case, however, one may have less complexes than reactions when some of the reactions have the same reactant complex.

It is important to observe, that the stoichiometric coefficients α_{ij} and β_{ij} in the Gorban description (3) both appear in matrix Y in different columns.

The structure of the set of reactions is usually depicted in a graphical form using the so-called reaction graph.

The reaction graph

The vertices V of the reaction graph $G = (V, E)$ correspond to the complexes, and the edges E to the reactions. Two complexes C_k and C_ℓ are connected by a directed edge, if a reaction in the form of

$$C_k \rightarrow C_\ell \tag{7}$$
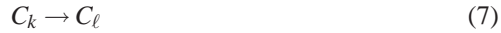
exists. Edge weights can be associated to the edges that are the reaction rate constants $k_{k\ell} > 0$, thus he reaction graph is a weighted directed graph. In this case the

set of *reaction vectors* can be defined as: $\mathscr{R} = \{\eta^{(l)} - \eta^{(k)} \mid C_k C_l \in E$ in $G\}$, where $\eta^{(i)}$ denotes the *i*th column of Y.

The *Kirchhoff matrix of the reaction graph* $A_k \in \mathbb{R}^{m \times m}$ uniquely describes the reaction graph with

$$[A_k]_{ij} = \begin{cases} -\sum_{l=1}^{m} k_{il} & \text{if } i = j \\ k_{ji} & \text{if } i \neq j \end{cases} \tag{8}$$

Because of construction, *the Kirchhoff matrix of the reaction graph is a column conservation matrix* with non-positive diagonal and non-negative off-diagonal, where the sum of the elements in a column is equal to zero. (We remark that the Kirchhoff matrix of weighted directed graphs is often defined as the negative transpose of A_k in the literature.)

Note, however, that the Kirchhoff matrix of the reaction graph does not uniquely determine the reaction kinetic system, since the information on the composition of the complexes is missing from the graph. A remedy of this situation is to associate weights to the vertices of the graph, as well. As vertices are associated to complexes, the corresponding column $\eta^{(j)}$ is associated to the vertex C_j.

The reaction equations

In order to construct the dynamic state equations of a reaction kinetic system, the information on the composition of the complexes that are coded in the stoichiometic matrix Y is also needed. The dynamic model that describes the evolution of the reaction kinetic system in its state spece is given by

$$\frac{dx}{dt} = Y \cdot A_k \cdot \varphi(x) = N \cdot \varphi(x) \tag{9}$$

It is important to note that the matrices Y and A_k uniquely determine the reaction kinetic system, because the stoichiometric coefficients in Y determine the reaction monomials in $\varphi(x)$.

2.2.3 The reaction simplex: positivity and linear invariants

Given the dynamic state equations of a reaction kinetic system in its Feinberg representation form (9), it is easy to show that the solution of it remains on a linear manifold, on the so-called *reaction simplex* determined by the initial conditions, assuming that all stoichiometric coefficients are non-negative (but not necessarily integers). Each vector $e \in \ker(N^T)$ generates a linear invariant for the system (5) since

$$e^T N = 0 \;\Rightarrow\; e^T \frac{dx}{dt} = 0 \;\Rightarrow\; e^T x(t) = const = e^T x_0$$

In order to show the positivity of the system, let us separate the production terms $P(x)$ from the desctruction terms $D(x)$ in Eq. (9) [14] by introducing the vector of reaction velocities $\omega_i(x) = k_i \varphi_i(x)$ to obtain:

$$P(x) = Y^{(\beta)} \omega(x) \ , \quad D(x) = \text{diag} \left(\frac{[Y^{(\alpha)} \omega(x)]_1}{x_1} ... \frac{[Y^{(\alpha)} \omega(x)]_n}{x_n} \right)$$

where $Y^{(\alpha)}$ is the sub-stochimetric matrix composed only from the α_{ij} coefficients of Eq. (1) while $Y^{(\beta)}$ is its corresponding β-pair. With the above notation, the dynamic state equations (9) become:

$$\frac{dx}{dt} = P(x) - D(x)x \tag{10}$$

where all non-zero entries of the diagonal matrix D_{ii} are polynomials (or generalized polynomials in the real stoichiometric coefficients case) in x because of the MAL kinetics. *Recall that all stochimetric coefficients and reaction rate constants are positive.* Then, if at a time moment τ all concentrations are non-negative ($x(\tau) \geq 0$) and the concentration of the species i is zero ($x_i(\tau) = 0$) then the corresponding time derivative will be non-negative, because the production term is non-negative, and the destruction term is zero which implies positivity of any state evolution starting from a positive initial point.

2.2.4 Example: A simple linear kinetics

Let us consider a simple reaction kinetic system shown in Fig. 1 consisting of two reversible first order steps and three components.

Fig. 1 Weighted reaction graph of a linear system
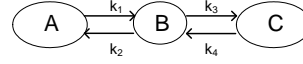
The dynamic state equations are as follows.

$$\begin{aligned}
\frac{dx_1}{dt} &= -k_1 x_1 + k_2 x_2 \\
\frac{dx_2}{dt} &= k_1 x_1 - k_2 x_2 - k_3 x_2 + k_4 x_3 \\
\frac{dx_3}{dt} &= k_3 x_2 - k_4 x_3
\end{aligned} \tag{11}$$

¿From this the Feinberg representation matrices and vectors are easy to derive

$$\varphi(x) = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}, \ Y = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \ N = A_k = \begin{bmatrix} -k_1 & k_2 & 0 \\ k_1 & -(k_2 + k_3) & k_4 \\ 0 & k_3 & -k_4 \end{bmatrix} \tag{12}$$

The system consists of only reversible reactions, thus the Gorban representation form also exists with $r = 2$ and

$$W(x) = \begin{bmatrix} -k_1 x_1 + k_2 x_2 \\ -k_3 x_2 + k_4 x_3 \end{bmatrix}, \; \mathcal{N} = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{bmatrix} \tag{13}$$

2.3 Stability

If the reaction kinetic system obeys the mass action law, then there exist easy-to-check necessary conditions of its global asymptotic stability.

2.3.1 Feinberg's approach

One of the most significant achievements in the study of the dynamical properties of complex chemical reaction systems is [6], where (among other important results) the global stability of so-called 'deficiency zero' reaction networks is proved with a given Lyapunov function.

The stability of reaction networks (5) can be examined using the notion of deficiency (see [6, 16]). It is an integer number which depends on the properties of matrix Y, and on the structure of the reaction graph G. The *deficiency* δ is defined as:

$$\delta = m - \ell - s \tag{14}$$

where m is the number of complexes and ℓ is the number of connected components in the reaction graph, while s is the dimension of the stoichiometric sub-space, i.e. $s = rank(\mathcal{R})$.

The deficiency zero theorem

If the reaction network is (weakly) reversible then there exists within each reaction simplex precisely one equilibrium, and that equilibrium is asymptotically stable if the dynamics is restricted to the reaction simplex to which the equilibrium point belongs. Consequently, the original system in the concentration space is globally stable in the positive orthant. Therefore, having zero deficiency is a very strong structural property.

It is important to note that the deficiency zero property is a structural feature of a certain class of reaction networks, therefore their stability does not depend on the system parameters.

2.3.2 Gorban's approach

In agreement with [6] (as they fall into the deficiency zero class) the closed and reversible reaction networks are proved to be globally stable ([2]). Here we generalize

this result for the class of reversible reaction kinetic systems with extended MAL kinetics, i.e. with real stochimetric coefficients.

Theorem 1. *Let the the dynamic state equation of a reaction kinetic system with reversible reactions be given in the form of (5), where* $\dim \ker(\mathcal{N}) = 0$. *Then the equilibrium point x^* of this system is globally stable with the Lyapunov function*

$$B_{x^*}(x) = \sum_{i=1}^{n} x_i \left(\ln \left(\frac{x_i}{x_i^*} \right) - 1 \right) + x_i^* \tag{15}$$

Proof. Define the auxiliary vector μ as

$$\mu(x) = [\ln(x_1), ..., \ln(x_1)]^T$$

and let us denote the jth column of the stociometric matrices $\mathcal{N}^{(\alpha)}$ by $\alpha^{(j)}$ and $\mathcal{N}^{(\beta)}$ by $\beta^{(j)}$, respectively. Let us use the following relations:

$$\mu^T \beta^{(j)} = \beta_1^{(j)} \ln(x_1) + ... + \beta_n^{(j)} \ln(x_n) = \ln \left(\frac{1}{k_j^-} x_1^{\beta_1^{(j)}} ... x_n^{\beta_n^{(j)}} \right) = \ln \left(\frac{1}{k_j^-} W_j^-(x) \right)$$

$$\mu^T \alpha^{(j)} = \ln \left(\frac{1}{k_j^+} W_j^+(x) \right) \tag{16}$$

Then the time-derivative of B_{x^*} can be computed as

$$\frac{dB_{x^*}}{dt} = \frac{\partial B_{x^*}}{\partial x} \mathcal{N} W(x) = (\mu - \mu^*)^T \sum_{j=1}^{r} (\beta^{(j)} - \alpha^{(j)})(W_j^+(x) - W_j^-(x)) \tag{17}$$

$$= \sum_{j=1}^{r} \left(\mu^T \beta^{(j)} - \mu^T \alpha^{(j)} - \mu^{*T} \beta^{(j)} + \mu^{*T} \alpha^{(j)} \right) (W_j^+(x) - W_j^-(x)) \tag{18}$$

$$= \sum_{j=1}^{r} \ln \left(\frac{W_j^-}{W_j^+} \right) (W_j^+(x) - W_j^-(x)) \leq 0 \tag{19}$$

and this completes the proof. □

2.3.3 Example of stability analysis: the simple linear kinetics

The simple reaction kinetic system with linear kinetics (see sub-section 2.2.4) is used here to illustrate the above method.

For the forthcoming calculations, let us assign the following values to the kinetic constants:

$$k_1 = 1, \ k_2 = 2, \ k_3 = 0.5, \ k_4 = 1$$

It can be easily checked that a basis vector for the equilibrium manifold is $v = [4 \ \ 2 \ \ 1]^T$. From this manifold, let us choose $x^* = [2 \ \ 1 \ \ 0.5]^T$ as an equilibrium

point of interest. Then, a quadratic and a logarithmic Lyapunov function can be constructed for the stability analysis of the system.

It can be computed that $P = \text{diag}([\frac{1}{4} \ \frac{1}{2} \ 1])$ is a solution for the following nonstrict linear matrix inequality (LMI):

$$A_k^T P + P A_k \leq 0$$

Therefore $V(x) = \frac{1}{4}x_1^2 + \frac{1}{2}x_2^2 + x_3^2$ is nonincreasing along the solutions of the system and proves stability in the linear sense.

Using **Theorem 1** we can construct the entropy-like Lyapunov function as

$$B_{x^*} = x_1 \ln\left(\frac{x_1}{2}\right) - x_1 + x_2 \ln(x_2) - x_2 + x_3 \ln(2x_3) - x_3 + 3.5$$

which is bounded from below, zero at x^*, convex in the positive orthant and non-increasing along the trajectories of the system. It's worth mentioning that we can define a dissipative-Hamiltonian structure [15] for the system in both the original coordinates (since it is a stable linear system) and, using a nonlinear coordinates transformation, in the "reaction space" [13].

3 Reaction kinetic systems as quasi-polynomial systems

The quasi-polynomial system class has been introduced as a general representation form of autonomous nonlinear systems with smooth nonlinearities (see e.g.[11], [12]).

Quasi-polynomial (QP) systems are systems of ODEs of the following form

$$\dot{x}_i = x_i \left(l_i + \sum_{j=1}^{m} [M]_{ij} \prod_{k=1}^{n} x_k^{[B]_{jk}} \right), \quad i = 1, \dots, n. \tag{20}$$

where $x \in \text{int}(\mathbb{R}_+^n)$, $M \in \mathbb{R}^{n \times m}$, $B \in \mathbb{R}^{m \times n}$, $l_i \in \mathbb{R}$, $i = 1, \dots, n$. Furthermore, $l = [l_1 \ \dots \ l_n]^T$. Without the loss of generality we can assume that $\text{Rank}(B) = n$ and $m \geq n$ (see [12]).

It is also known that the class of QP systems is closed onder the so-called *quasi-monomial (QM) transformation*:

$$x_i' = \prod_{k=1}^{n} x_k^{C_{ik}} \tag{21}$$

where $C \in \mathbb{R}^{n \times n}$ is an invertible matrix. The transformed system matrices are $M' = C^{-1} \cdot M$, $B' = B \cdot C$, $l' = C^{-1} \cdot l$, and the product $\mathscr{A} = BM = B'M'$ is invariant under the QM transformation.

3.1 The Lotka-Volterra canonical form

Let us denote the *monomials* of (20) as

$$z_j = \prod_{k=1}^{n} x_k^{[B]_{jk}}, \quad j = 1, \ldots, m. \tag{22}$$

Let $z = [z_1 \ z_2 \ \ldots \ z_m]^T$. It can be easily calculated that the time derivatives of the monomials form a Lotka-Volterra (LV) system i.e.

$$\dot{z}_i = z_i(\lambda_i + \sum_{j=1}^{m} [\mathscr{A}]_{ij} \cdot z_j), \quad i = 1, \ldots, m \tag{23}$$

where $\mathscr{A} = B \cdot M \in \mathbb{R}^{m \times m}$, $\lambda = B \cdot l \in \mathbb{R}^{m \times 1}$, $\lambda_i = [\lambda]_i$, and $z_i > 0$, i=1,..., m.

We note that the matrix $\mathscr{A}$ of an LV system originating from a QP system is often rank deficient since the number of monomials is larger than the number of QP variables in many cases. It is visible that LV systems form a proper subset of QP systems with B being the unit matrix of size $m \times m$ and the matrix $\mathscr{A}$ is the invariant of the QP system class.

It is often useful to represent (23) in its *homogeneous* form. This form can be obtained by introducing a new variable z_{m+1}, such that $\dot{z}_{m+1} = 0$ and $z_{m+1}(0) = 1$. Using the new variable, (23) can be written as

$$\dot{z}_i = z_i \left(\sum_{j=1}^{m+1} [E]_{ij} z_j \right), \quad i = 1, \ldots, m+1 \tag{24}$$

with

$$E = \begin{bmatrix} \mathscr{A} & \lambda \\ 0 & 0 \end{bmatrix} \tag{25}$$

3.2 QP and LV realization of reaction kinetic systems with MAL kinetics illustrated by the simple linear kinetics example

It has already been shown [11] that the reaction kinetic system class is a special case of the QP system class, so every reaction kinetic system model has its QP form, and consequently, it can be transformed to a LV form. The properties of such transformations are illustrated here using the siple linear kinetics example given in sub-section 2.2.4.

The QP-ODEs are derived from the dynamic state equations (11)

$$\begin{aligned} \frac{dx_1}{dt} &= x_1 \cdot \left(-k_1 + k_2 x_1^{-1} x_2 \right) \\ \frac{dx_2}{dt} &= x_2 \cdot \left(-(k_2 + k_3) + k_1 x_2^{-1} x_1 + k_4 x_2^{-1} x_3 \right) \\ \frac{dx_3}{dt} &= x_3 \cdot \left(-k_4 + k_3 x_2 x_3^{-1} \right) \end{aligned} \tag{26}$$

Thus we have four quasi-monomials

$$x_1^{-1}x_2, x_1x_2^{-1}, x_2^{-1}x_3, x_2x_3^{-1}$$

This gives rise to the following QP representation matrices and vectors

$$l = \begin{bmatrix} -k_1 \\ -(k_2+k_3) \\ -k_4 \end{bmatrix}, \ M = \begin{bmatrix} k_2 & 0 & 0 & 0 \\ 0 & k_1 & k_4 & 0 \\ 0 & 0 & 0 & k_3 \end{bmatrix}, \ B = \begin{bmatrix} -1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & -1 & 1 \\ 0 & 1 & -1 \end{bmatrix} \tag{27}$$

Finally, the following LV representation vector and matrix are resulted

$$\lambda = \begin{bmatrix} -k_1+(k_2+k_3) \\ k_1-(k_2+k_3) \\ (k_2+k_3)-k_4 \\ -(k_2+k_3)+k_4 \end{bmatrix}, \ \mathscr{A} = \begin{bmatrix} -k_2 & k_1 & k_4 & 0 \\ k_2 & -k_1 & -k_4 & 0 \\ 0 & -k_1 & -k_4 & k_3 \\ 0 & k_1 & k_4 & -k_3 \end{bmatrix} \tag{28}$$

3.3 Reaction kinetic realization of QP systems

The reaction kinetic realization of a QP system can be developed and its existence checked following the steps that are described in this sub-section.

Transformation into a pre-Feinberg form

$$\frac{dx}{dt} = \mathscr{M}\varphi(x) \tag{29}$$

First the reaction monomials can be determined form the multi-set

$$\overline{\mathscr{S}}_\varphi = \{x_1, ..., x_n, \ x_1 \cdot z_1, ..., x_1 \cdot z_m, ..., \ x_n \cdot z_1, ..., x_n \cdot z_m\} \tag{30}$$

such that the identical elements should only be taken once, and the monomials with zero coefficients (either in l_i or in $[M]_{ij}$) should be omitted. ¿From this normalized set of reaction monomials the Feinberg stoichiometric matrix Y can be easily determined.

The coefficient matrix $\mathscr{M}$ can thereafter be computed by rearranging the original QP model coefficients in the vector l and matrix M. If one puts the linear reaction monomials x_i first in the vector $\varphi(x)$, then there will be an $n \times n$ diagonal block in $\mathscr{M}$:

$$\mathscr{M} = [Diag(l_i, i = 1, ..., n) \mid \mathscr{M}_M] \tag{31}$$

Computing the reaction kinetic realization matrices

The feasibility of the reaction kinetic realization and the computation of the missing A_k coefficient matrix is performed using the dynamic state equation form of the Feinberg realization in Eq. (9). According to this, the above determined QP coefficient matrix $\mathcal{M}$ and stochimetric matrix Y is in the following relationship:

$$\mathcal{M} = Y \cdot \hat{A}_k \tag{32}$$

from which the unknown coefficient matrix $\hat{A}_k$ can be determined by using the pseudo-inverse of Y if the columns of Y are linearly independent:

$$\hat{A}_k = Y^+ \cdot \mathcal{M} \tag{33}$$

If the number of complexes are greater than the number of species and therefore the columns of Y cannot be linearly independent, then (32) becomes an underdetermined system of linear equations for which such an $\hat{A}_k$ solution might be sought that is a column conservation matrix.

Theorem 2. *A reaction kinetic realization exists, if the resulting coefficient matrix $\hat{A}_k$ is a column conservation matrix, i.e. a matrix with non-positive diagonal and non-negative off-diagonal elements and with column sum equal to zero.*

3.4 Reaction kinetic realization of LV systems

As an LV system is a canonical representation form of a QP one, the question of the existence of a reaction kinetic realization of a LV system is of great theoretical importance. In addition, some of the parameter estimation methods for infererring reation mechanisms from measured data use the possible reaction monomials of all possible second order reaction steps as basis functions, see [1].

The structure of the pre-Feinberg representation

Assume to have a LV model given in its homogeneous form (24). Then the reaction monomials, i.e. the entries of the vector $\varphi(z)$ are in the form of $z_i z_j$ with $i, j = 1, ..., m+1$ and with the $(m+1)$th variable being a constant 1. We can arrange the reaction monomials in their lexicographical order with identifying the $(m+1)$th element to the 0th one to create the following ordering

$$z_1, z_2, ..., z_m, \ z_1 z_1, z_1 z_2, ..., z_1 z_m, ...$$

then the stoichiometric matrix Y has a following simple structure

$$Y = \begin{bmatrix} 1\ 0\ 0\ ...\ 0 & 2\ 1\ 1\ ...\ 1 & 0\ 0\ 0\ ...\ 0 & ... \\ 0\ 1\ 0\ ...\ 0 & 0\ 1\ 0\ ...\ 0 & 2\ 1\ 1\ ...\ 1 & ... \\ 0\ 0\ 1\ ...\ 0 & 0\ 0\ 1\ ...\ 0 & 0\ 1\ 0\ ...\ 0 & ... \\ ..\ ..\ ..\ ...\ 0 & ..\ ..\ ..\ ...\ 0 & ..\ ..\ ..\ ...\ 0 & ... \\ 0\ 0\ 0\ 0\ 1 & 0\ 0\ 0\ 0\ 1 & 0\ 0\ 0\ 0\ 1 & ... \end{bmatrix} \tag{34}$$

The coefficient matrix N has a similar structure but it contains the elements of the matrix $\mathscr{A}$ and the vector λ

$$N = \begin{bmatrix} \lambda_1\ 0\ 0\ ...\ 0 & a_{11}\ a_{12}\ a_{13}\ ...\ a_{1m} & 0\ \ 0\ \ 0\ ...\ \ 0 & ... \\ 0\ \lambda_2\ 0\ ...\ 0 & 0\ a_{21}\ 0\ \ ...\ \ 0 & a_{22}\ a_{23}\ a_{24}\ ...\ a_{2m} & ... \\ 0\ \ 0\ \ 1\ ...\ 0 & 0\ \ 0\ a_{31}\ ...\ \ 0 & 0\ \ a_{32}\ 0\ \ ...\ \ 0 & ... \\ ..\ ..\ ..\ ...\ 0 & ..\ \ \ ..\ \ \ ..\ \ ...\ \ 0 & ..\ \ \ \ ..\ \ \ \ ..\ \ ...\ \ 0 & ... \\ 0\ \ 0\ \ 0\ \ 0\ \lambda_m & 0\ \ \ 0\ \ \ 0\ \ \ 0\ a_{m1} & 0\ \ \ \ 0\ \ \ \ 0\ \ \ \ 0\ a_{m2} & ... \end{bmatrix} \tag{35}$$

where the notation $[\mathscr{A}_{ij}] = a_{ij}$ is applied.

The existence of reaction kinetic realization of 2nd order LV systems

Let us consider the simplest non-trivial case of LV systems when $n = 2$ and the model is in the following form

$$\begin{aligned} \dot{z}_1 &= \lambda_1 z_1 + a_{11} z_1^2 + a_{12} z_1 z_2 \\ \dot{z}_2 &= \lambda_2 z_2 + a_{22} z_2^2 + a_{21} z_1 z_2 \end{aligned} \tag{36}$$

Then the pre-Feinberg realization matrices are

$$Y = \begin{bmatrix} 1\ 0\ 2\ 1\ 0 \\ 0\ 1\ 0\ 1\ 2 \end{bmatrix}, \quad N = \begin{bmatrix} \lambda_1\ 0\ a_{11}\ a_{12}\ 0 \\ 0\ \lambda_2\ 0\ a_{21}\ a_{22} \end{bmatrix} \tag{37}$$

Instead of solving Eq. (33) that has multiple solutions in this case, let us use the physical picture behind the terms in the reaction equations to find possible complexes and reaction steps compatible with the terms in Eq. (36).

Admissible complexes If we denote by A and B the components the concentration of which is denoted by z_1 and z_2, respectively, then the following complexes can appear in the reaction system corresponding to Eq. (36):
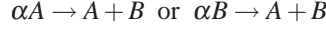
$$A,\ B,\ 2A,\ A + B,\ 2B \tag{38}$$

Incompatible reaction types Next we observe that any reaction in the form of

$$\alpha_i \mathbf{X}_i \rightarrow \beta_j \mathbf{X}_j \ (i \neq j)$$
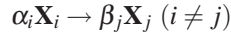
with $\alpha_i, \beta_j \in \{1, 2\}$ and $\mathbf{X}_i, \mathbf{X}_j \in \{A, B\}$ gives rise to a term in

$$\frac{dz_j}{dt} = ... + k_{ij} z_i^{\alpha_i} + ...$$

that is not compatible with the right-hand side structure of Eq. (36), where every term on the right-hand side of $\frac{dz_j}{dt}$ should contain a factor z_j. Because of the same reason, any reaction in the form

$$\alpha A \rightarrow A + B \quad \text{or} \quad \alpha B \rightarrow A + B$$

with $\alpha \in \{1, 2\}$ cannot appear in any reaction kinetic realization of LV models.

Reaction graph superstructure ¿From the remaining reaction types defined over the set of possible complexes in Eq. (38), the reaction graph superstructure seen in Fig. 2 can be obained. The Kirchhoff matrix of the reaction graph in Fig. 2 (follow-
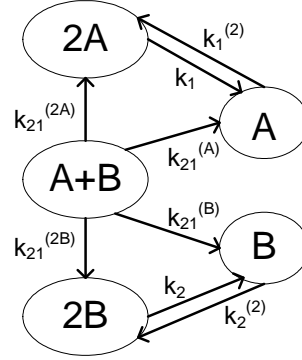
Fig. 2 Weighted reaction graph superstructure for the 2nd order LV model

ing the order of complexes in (38)) is:

$$A_k = \begin{bmatrix} -k_1^{(2)} & 0 & k_1 & k_{12}^{(A)} & 0 \\ 0 & -k_2^{(2)} & 0 & k_{12}^{(B)} & k_2 \\ k_1^{(2)} & 0 & -k_1 & k_{12}^{(2A)} & 0 \\ 0 & 0 & 0 & -K & 0 \\ 0 & k_2^{(2)} & 0 & k_{12}^{(2A)} & -k_2 \end{bmatrix} \tag{39}$$

where $K = k_{12}^{(A)} + k_{12}^{(B)} + k_{12}^{(2A)} + k_{12}^{(2B)}$. Multiplying the above matrix A_k with the stoichiometric matrix Y in Eq. (37), we obtain the following coefficient matrix:

$$N = \begin{bmatrix} k_1^{(2)} & 0 & -k_1 & -k_{12}^{(B)} + k_{12}^{(2A)} - k_{12}^{(2B)} & 0 \\ 0 & k_2^{(2)} & 0 & -k_{12}^{(A)} - k_{12}^{(2A)} + k_{12}^{(2B)} & -k_2 \end{bmatrix} \tag{40}$$

Comparing the matrix elements of the coefficient matrices in Eqs. (40) and (37), the following necessary conditions for the existence of a reaction kinetic realization are obtained:

$$\lambda_1 \geq 0 \ , \ \lambda_2 \geq 0 \ , \ a_{11} \leq 0 \ , \ a_{22} \leq 0 \tag{41}$$

There are no restrictions for the coefficients a_{12} and a_{21}.

In addition we can see, that *the reaction kinetic realization is not unique*, because the coefficients a_{12} and a_{21} determine four reaction rate constants $k_{12}^{(A)}$, $k_{12}^{(2A)}$, $k_{12}^{(2B)}$ and $k_{12}^{(B)}$.

Positivity of the equilibrium point of 2nd order LV systems with reaction kinetic realization

The positivity of any second order LV system that admits a reaction kinetic realization is guaranteed by the positivity property of reaction kinetic systems [14]. However, the uniqueness and the strict positivity of the equilibrium point of the system is also of interest, that will be investigated here.

Let us denote the determinant of the LV coefficient matrix $\mathscr{A}$ by

$$d = \det \mathscr{A} = \det \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = a_{11}a_{22} - a_{12}a_{21} \tag{42}$$

¿From Eq. (36) the following equilibrium point is obtained when $d \neq 0$

$$z_1^* = \frac{a_{12}\lambda_2 - a_{22}\lambda_1}{d} \quad , \quad z_2^* = \frac{a_{21}\lambda_1 - a_{11}\lambda_2}{d} \tag{43}$$

It can be seen that a *necessary condition for having a positive equilibrium point is to have either $\lambda_1 \neq 0$ or $\lambda_2 \neq 0$ or none of them equal to zero.*

If *in addition the LV coefficient matrix $\mathscr{A}$ is a column conservation matrix*, i.e.

$$a_{12} \geq 0 \quad , \quad a_{21} \geq 0 \quad , \quad |a_{11}| \geq a_{21} \quad , \quad |a_{22}| \geq a_{12}$$

then the equilibrium point (z_1^*, z_2^*) is strictly positive keeping in mind the conditions of having a reaction kinetic realization given in Eq. (41).

Reaction kinetic realization of general LV systems

Now we are ready to generalize the results presented before to the general, mth order case.

Admissible complexes It can be seen from the general LV equation form (23), that the following complexes can appear in the reaction system:

$$\{\mathbf{X}_i, \ i = 1, ..., m\}, \ \{2\mathbf{X}_i, \ i = 1, ..., m\}, \ \{\mathbf{X}_i + \mathbf{X}_j, \ i, j = 1, ..., m, \ i \neq j\} \tag{44}$$

¿From this we construct the reaction monomial vector $\varphi(z)$ as follows:

$$\varphi(z) = \left[z_1, ..., z_m, \ z_1^2, ..., z_m^2, \ z_1 z_2, ..., z_{m-1} z_m \right]^T \tag{45}$$

Incompatible reaction types Besides of the incompatible reaction types described before, one also has to consider the reaction type
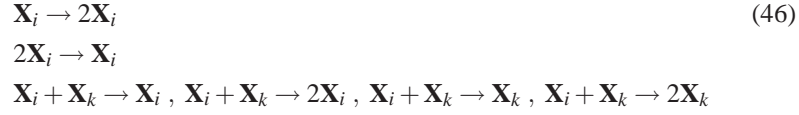
$$\mathbf{X}_i + \mathbf{X}_k \rightarrow \mathbf{X}_j + \mathbf{X}_\ell$$
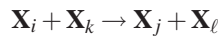
This reaction gives rise to a term in

$$\frac{dz_j}{dt} = \ldots + k_{ik,j\ell} z_i z_k + \ldots$$

that is not compatible with the right-hand side structure of Eq. (23), where every term on the right-hand side of $\frac{dz_j}{dt}$ should contain a factor z_j.

Therefore, only the following reaction types are admissible in the reaction graph of an LV model:

$$\mathbf{X}_i \to 2\mathbf{X}_i \tag{46}$$
$$2\mathbf{X}_i \to \mathbf{X}_i$$
$$\mathbf{X}_i + \mathbf{X}_k \to \mathbf{X}_i \ , \ \mathbf{X}_i + \mathbf{X}_k \to 2\mathbf{X}_i \ , \ \mathbf{X}_i + \mathbf{X}_k \to \mathbf{X}_k \ , \ \mathbf{X}_i + \mathbf{X}_k \to 2\mathbf{X}_k$$

Reaction graph superstructure ¿From the above possible reaction types it follows, that both the vertices $\mathbf{X}_i$ and $2\mathbf{X}_i$ have out-degree equal to one, while the vertices $\mathbf{X}_i + \mathbf{X}_k$ have out-degree equals four. This implies that the column-structure of the Kirchhoff matrix of the reaction graph follows that of the 2-dimensional case (see Eq. (39)), but now we have to fill all elements of a column with zeros except of two non-zero elements corresponding to the outward directed edges from the complexes $\mathbf{X}_i$ and $2\mathbf{X}_i$ or four non-zero elements for the complexes $\mathbf{X}_i + \mathbf{X}_k$.

As an example, the weighted reaction graph superstructure for the 3rd order LV model in Fig. 3 shows that the graph is the union of the 2-dimensional superstructures (seen in Fig. 2).
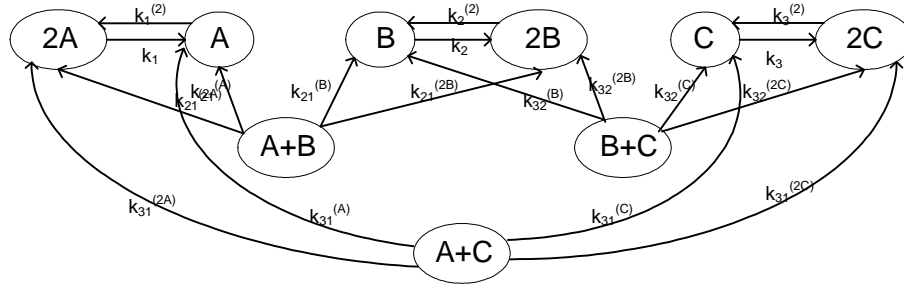
Fig. 3 Weighted reaction graph superstructure for the 3rd order LV model

Therefore, similarly to the two-dimensional case, the following necessary conditions can be given for a LV model to have a reaction kinetic realization:

$$\lambda_i \geq 0, \ A_{ii} \leq 0, \ i = 1, \ldots, m \tag{47}$$

There are no restrictions for the coefficients A_{ij} when $i \neq j$.

In addition we can see, that *the reaction kinetic realization is not unique*, because the coefficients A_{ij} and A_{ji} determine four reaction rate constants $k_{ij}^{(\mathbf{X}_i)}$, $k_{ij}^{(2\mathbf{X}_i)}$, $k_{ij}^{(2\mathbf{X}_j)}$ and $k_{ij}^{(\mathbf{X}_j)}$.

4 Conclusion

The algebraic and stability properties of the reaction kinetic system class, being a special sub-class of positive systems have been investigated in this paper. The original notion based on the kinetical equations obeying mass action law has been generalized to cover the cases with real exponents in the reaction monomials. It has been shown that the generalized class still possesses the same stability property under the usual Lyapunov function.

Thereafter the relationship between the reaction kinetic and the quasi-polynomial (QP) systems classes is established based on their algebraic characterization, and a method is proposed to test if a QP system has a generalized reaction kinetic realization. Simple algebraic conditions are also given for general Lotka-Volterra systems that guarantee the existence of theeir reaction kinetic model form.

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