

A Deficiency Zero Theorem for a Class of Power–Law Kinetic Systems with Non–Reactant–Determined Interactions

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Abstract

The Deficiency Zero Theorem (DZT) provides definitive results about the dynamical behavior of chemical reaction networks with deficiency zero. Thus far, the available DZTs only apply to classes of power-law kinetic systems with reactant-determined interactions (i.e., the kinetic order vectors of the branching reactions of a reactant complex are identical). In this paper, we present the first DZT valid for a class of power-law systems with non-reactant-determined interactions (i.e., there are reactant complexes whose branching reactions have different kinetic order vectors). This class of power-law systems is characterized here by a decomposition into subnetworks with specific properties of their stoichiometric and reactant subspaces, as well as their kinetics. We illustrate our results to a power-law system of a pre-industrial carbon cycle model, from which we abstracted the properties of the above-mentioned decomposition. Specifically, our DZT is applied to a subnetwork of the carbon cycle system to describe the subnetwork's steady states. It is also shown that the qualitative dynamical properties of the subnetwork may be lifted to the entire network of pre-industrial carbon cycle.

1 Introduction

Chemical reaction networks (CRNs) are ubiquitous in many areas of studies, notably in biochemistry-related disciplines. They provide a graphical form of the dynamical system of networks of interacting species [23]. Abstractly, a CRN represents a universe whose evolution corresponds to the transformation of its chemical elements – i.e., the consumption of its elements to generate others [20]. Hence, in theory, systems with similar network structures, even in areas beyond the natural sciences, may be represented by CRNs [20,23].

The study of CRNs gave rise to a significant body of theoretical work, notably the so-called *Chemical Reaction Network Theory (CRNT)*. The field had its foundation from the papers of F. Horn, M. Feinberg, and R. Jackson in 1972 [4,9,10]. Results in CRNT reveal that for many CRNs, their structure and associated kinetics (i.e., reaction rate functions) alone determine the dynamical properties of the system. This is interesting, since the structure (nor the kinetics) itself does not carry any information about the parameter values and initial quantities. CRNT asserts that CRNs that satisfy certain structural conditions exhibit a similar type of qualitative dynamical behavior.

Early results in CRNT revolved around the classification of a CRN using a non-negative integer called the *deficiency* [5–7]. This index is not dependent on the network’s size. Very large or complex CRNs may, in fact, have zero deficiency [17]. Instead, the deficiency measures the amount of ‘linear independence’ among the reactions – the higher the deficiency, the lower the extent of linear independence [16]. Hence, deficiency-zero CRNs possess the highest possible degree of linear independence among the reactions.

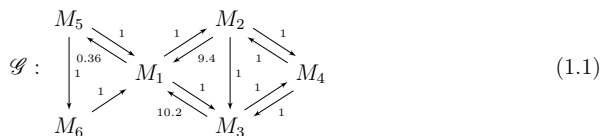
The Deficiency Zero Theorem (DZT) establishes decisive results about the nature of dynamics that deficiency-zero networks possess. All DZTs known to date are valid for power-law kinetic systems with reactant-determined interactions (denoted by “PL-RDK”), which are kinetic systems with power-law rate functions whose kinetic order vectors are identical for reactions with the same reactant complex. The first DZT asserts that all weakly reversible (i.e., each reaction is part of a cycle) deficiency-zero networks taken with mass-action kinetics (MAK), regardless of the positive rate constants, cannot admit multiple positive steady states, unstable positive equilibrium or sustained oscillations [5–7]. Note that in mass-action kinetics, the kinetic orders are the stoichiometric coefficients of the reactant complex and hence, MAK is a special case of PL-RDK.

The next DZT was published some 40 years later by S. Müller and G. Regensburger pa-

pers on Generalized Mass Action Kinetic (GMAK) systems, which marked the emergence of results on power-law kinetics in CRNT [12, 13]. GMAK systems essentially correspond to PL-RDK systems, but there are some slight differences (see Section 6 of [18] for a detailed discussion). Müller and Regensburger introduced the notion of *kinetic deficiency*, which was the basis of their *Kinetic Deficiency Zero Theorem*.

In [19], Talabis et al. derived a Deficiency Zero and a Deficiency One Theorem for a class of power-law systems (denoted by “PL-TIK”) with linkage class-wise linear independent interactions. It is shown that any weakly reversible PL-TIK systems have zero kinetic deficiency. Hence, the Deficiency Zero Theorem in [18] turns out to be a special case of the Müller-Regensburger result.

The following CRN \mathcal{G} is weakly reversible and has deficiency zero with power-law kinetics (the arc labels are the kinetic orders):



Does this system have positive equilibria? One may immediately think of applying a DZT. However, observe that there are branching reactions (e.g., $M_1 \rightarrow M_2$ and $M_1 \rightarrow M_5$) with different kinetic orders. This power-law kinetic system is said to have non-reactant-determined interactions (denoted by “PL-NDK”). First examples of models of biological systems displaying this type of power-law kinetics (but with higher deficiencies) were provided by Arceo et al. in [1, 3]. The network \mathcal{G} , in fact, points to the CRN representation of a power-law approximation of the Earth’s pre-industrial carbon cycle model of R. Schmitz [15]. For systems such as \mathcal{G} , existing DZTs are not applicable.

However, it can be shown that \mathcal{G} has an interesting network decomposition: it is the union of subnetworks that have no common reactions on pairwise basis. The interesting property is that the kinetics on each subnetwork is of a PL-RDK subclass for which a DZT is known. This observation led us to a DZT that aids the description of the steady states of \mathcal{G} . Moreover, to our knowledge, the result is the first DZT which is valid for a class of PL-NDK systems.

The rest of the paper is organized as follows. Section 2 reviews important concepts and results in CRNT relevant to this paper. Section 3 discusses our main result – a Deficiency Zero Theorem beyond PL-RDK systems. This theorem is applied to a subnetwork of

the power-law kinetic system corresponding to the pre-industrial carbon cycle model of Schmitz. It is shown that the qualitative dynamical behavior of this network carries over to the entire network of pre-industrial carbon cycle. In Section 4, we summarize our results and outline some research perspectives.

2 Fundamentals of Chemical Reaction Networks and Kinetic Systems

This section reviews notions, results and notations (obtained from [3, 18]) that are pertinent in understanding the results in this work. Some concepts introduced by Feinberg in [5, 7] are also reviewed.

Notation. We denote the real numbers by \mathbb{R} , the non-negative real numbers by $\mathbb{R}_{\geq 0}$ and the positive real numbers by $\mathbb{R}_{> 0}$. Objects in the reaction systems are viewed as members of vector spaces. Suppose \mathcal{S} is a finite index set. By $\mathbb{R}^{\mathcal{S}}$, we mean the usual vector space of real-valued functions indexed by \mathcal{S} . For $x \in \mathbb{R}^{\mathcal{S}}$, the i^{th} coordinate of x is denoted by x_i , where $i \in \mathcal{S}$. The sets $\mathbb{R}_{\geq 0}^{\mathcal{S}}$ and $\mathbb{R}_{> 0}^{\mathcal{S}}$ are called the *non-negative* and *positive orthants* of $\mathbb{R}^{\mathcal{S}}$, respectively. Addition, subtraction, and scalar multiplication in $\mathbb{R}^{\mathcal{S}}$ are defined in the usual way. If $x \in \mathbb{R}_{> 0}^{\mathcal{S}}$ and $y \in \mathbb{R}^{\mathcal{S}}$, we define $x^y \in \mathbb{R}_{> 0}$ by

$$x^y = \prod_{i \in \mathcal{S}} x_i^{y_i}. \quad (2.1)$$

The vector $\log x \in \mathbb{R}^{\mathcal{S}}$, where $x \in \mathbb{R}_{> 0}^{\mathcal{S}}$, is given by $(\log x)_i = \log x_i$, for all $i \in \mathcal{S}$. If $x, y \in \mathbb{R}^{\mathcal{S}}$, the standard scalar product $x \cdot y \in \mathbb{R}$ is defined by $x \cdot y = \sum_{i \in \mathcal{S}} x_i y_i$. By the *support* of $x \in \mathbb{R}^{\mathcal{S}}$, denoted by $\text{supp } x$, we mean the subset of \mathcal{S} assigned with non-zero values by x . That is, $\text{supp } x := \{i \in \mathcal{S} \mid x_i \neq 0\}$.

We formally define CRN as a digraph with vertex-labelling (its stoichiometry).

Definition 1. A **chemical reaction network** is a digraph $(\mathcal{C}, \mathcal{R})$ where each vertex has positive degree and stoichiometry, i.e. there is a finite set \mathcal{S} (whose elements are called **species**) such that \mathcal{C} is a subset of $\mathbb{R}_{\geq 0}^{\mathcal{S}}$. Each vertex is called a **complex** and its coordinates in $\mathbb{R}_{\geq 0}^{\mathcal{S}}$ are called **stoichiometric coefficients**. The arcs are called **reactions**. We denote the number of species with m , the number of complexes with n and the number of reactions with r .

This definition of a chemical reaction network is equivalent to the usual definition as a triple $\mathcal{N} = (\mathcal{S}, \mathcal{C}, \mathcal{R})$ in [5] with the requirement $\mathcal{S} = \bigcup \text{supp } y$ for $y \in \mathcal{C}$, i.e. each species appears in at least one complex.

In the reaction $y \rightarrow y'$, we say that y is the **reactant** complex and y' is the **product** complex. Two useful maps are associated with each reaction – the reactant map and the product map. The **reactant map** $\rho : \mathcal{R} \rightarrow \mathcal{C}$ maps a reaction to its reactant complex while the **product map** $\pi : \mathcal{R} \rightarrow \mathcal{C}$ maps it to its product complex. We denote $|\rho(\mathcal{R})|$ with n_r , i.e. the number of reactant complexes.

A connected component of a CRN is called a **linkage class**, and the number of linkage classes in the network is denoted by ℓ . A CRN is **weakly reversible** if whenever there exists a directed path from a complex y to a complex y' , there also exists a directed path from y' to y .

Suppose the set $\{\omega_i \in \mathbb{R}^{\mathcal{S}} \mid i \in \mathcal{S}\}$ forms the standard basis for $\mathbb{R}^{\mathcal{S}}$ where $\mathcal{S} = \mathcal{S}, \mathcal{C}$ or \mathcal{R} . We recall three maps relevant in the study of CRNs: incidence map, map of complexes, and stoichiometric map.

Definition 2. Let $\mathcal{N} = (\mathcal{S}, \mathcal{C}, \mathcal{R})$ be a CRN. The **map of complexes** $Y : \mathbb{R}^{\mathcal{C}} \rightarrow \mathbb{R}^{\mathcal{S}}$ maps the basis vector ω_i to the complex $i \in \mathcal{C}$. The **incidence map** $I_a : \mathbb{R}^{\mathcal{R}} \rightarrow \mathbb{R}^{\mathcal{C}}$ is the linear map defined by mapping for each reaction $r : i \rightarrow j \in \mathcal{R}$, the basis vector ω_r to the vector $\omega_j - \omega_i \in \mathcal{C}$. The **stoichiometric map** $N : \mathbb{R}^{\mathcal{R}} \rightarrow \mathbb{R}^{\mathcal{S}}$ is defined as $N = Y \circ I_a$.

$\text{Im } N$ is called the **stoichiometric subspace** S , whose dimension s is called the **rank** of the CRN. Two vectors $c, c' \in \mathbb{R}^{\mathcal{S}}$ are **stoichiometrically compatible** if $c - c' \in S$. The intersection of a coset $c + S$ with $\mathbb{R}_{\geq 0}^{\mathcal{S}}$ is called a **stoichiometric compatibility class**.

A non-negative integer, called the *deficiency*, can be associated to each CRN. This number has been the center of many studies in CRNT due to its relevance in the dynamic behavior of the system.

Definition 3. The **deficiency** of a CRN is the integer $\delta = n - \ell - s$.

The **reactant matrix** Y_{res} is the $m \times n_r$ matrix Y without the columns of the non-reactant complexes (i.e., those complexes that are purely product complexes). Its columns are the reactant complexes. Its image $\text{Im } Y_{\text{res}}$ is called the **reactant subspace** R , whose dimension q is called the **reactant rank** of the CRN. The concept of reactant deficiency was introduced by Arceo et al. in [2]:

Definition 4. The **reactant deficiency** $\delta_\rho := n_r - q$, i.e., the difference between the number of reactant complexes and the reactant rank q .

Remark 1. Theorem 1 of [2] summarizes the relationship between the deficiency and reactant deficiency of a CRN. In particular, for weakly reversible networks, $0 \leq \delta_\rho - \delta \leq \ell$.

By *kinetics* of a CRN, we mean the assignment of a rate function to each reaction in the CRN. It is defined formally as follows.

Definition 5. A **kinetics** of a CRN $\mathcal{N} = (\mathcal{S}, \mathcal{C}, \mathcal{R})$ is an assignment of a rate function $K_j : \Omega_K \rightarrow \mathbb{R}_{\geq 0}$ to each reaction $j \in \mathcal{R}$, where Ω_K is a set such that $\mathbb{R}_{>0}^{\mathcal{S}} \subseteq \Omega_K \subseteq \mathbb{R}_{\geq 0}^{\mathcal{S}}$, $c \wedge d \in \Omega_K$ whenever $c, d \in \Omega_K$, and

$$K_j(c) \geq 0, \quad \text{for all } c \in \Omega_K.$$

A kinetics for a network \mathcal{N} is denoted by $K = [K_1, K_2, \dots, K_r]^\top : \Omega_K \rightarrow \mathbb{R}_{\geq 0}^{\mathcal{R}}$. The pair (\mathcal{N}, K) is called the **chemical kinetic system (CKS)**.

The above definition is adopted from [23]. It is expressed in a more general context than what one typically finds in CRNT literature. Note that for power-law kinetic systems, one sets $\Omega_K = \mathbb{R}_{>0}^{\mathcal{S}}$. Here, we focus on the kind of kinetics relevant to our context:

Definition 6. A **chemical kinetics** is a kinetics K satisfying the positivity condition:

$$\text{For each reaction } j : y \rightarrow y' \in \mathcal{R}, K_j(c) > 0 \text{ if and only if } \text{supp } y \subset \text{supp } c.$$

Once a kinetics is associated with a CRN, we can determine the rate at which the concentration of each species evolves at composition c .

Definition 7. The **species formation rate function (SFRF)** of a chemical kinetic system (CKS) is the vector field

$$f(x) = NK(x) = \sum_{y \rightarrow y'} K_{y \rightarrow y'}(x)(y' - y). \quad (2.2)$$

The equation $dx/dt = f(x)$ is the **ODE or dynamical system** of the CKS. A **positive equilibrium or steady state** x is an element of $\mathbb{R}_{>0}^{\mathcal{S}}$ for which $f(x) = 0$. The set of positive equilibria of a chemical kinetic system is denoted by $E_+(\mathcal{N}, K)$. For a differentiable f , a steady state x is called **non-degenerate** if $\text{Ker}(J_x(f)) \cap S = \{0\}$, where $J_x(f)$ is the Jacobian matrix of f at x .

Power-law kinetics is defined by an $r \times m$ matrix $F = [F_{ij}]$, called the **kinetic order matrix**, and vector $k \in \mathbb{R}^{\mathcal{R}}$, called the **rate vector**.

Definition 8. A kinetics $K : \mathbb{R}_{>0}^{\mathcal{S}} \rightarrow \mathbb{R}^{\mathcal{R}}$ is a **power-law kinetics (PLK)** if

$$K_i(x) = k_i x^{(F_{i,\cdot})^\top} \quad \text{for } i = 1, \dots, r, \quad (2.3)$$

where $k_i \in \mathbb{R}_{>0}$ and $F_{i,\cdot}$ refers to the i^{th} row of the kinetic order matrix F . A PLK system has **reactant-determined kinetics** (of type **PL-RDK**) if for any two reactions i, j with identical reactant complexes, the corresponding rows of kinetic orders in F are identical, i.e., $F_{ik} = F_{jk}$ for $k = 1, \dots, m$. On the other hand, a PLK system has **non-reactant-determined kinetics** (of type **PL-NDK**) if there exist two reactions with the same reactant complexes whose corresponding rows of kinetic orders in F are not identical.

Note that in Equation (2.3), the vector $x^{(F_{i,\cdot})^\top} \in \mathbb{R}^{\mathcal{R}}$ is computed using Equation (2.1).

Remark 2. Clearly, mass-action kinetics is a special case of PL-RDK. For mass-action, the corresponding kinetic order matrix is formed by taking F_{ij} to be the stoichiometric coefficient of the species j in the reactant complex of reaction i .

Recall the definition of the $m \times n$ matrix \tilde{Y} from [13]: For a reactant complex, the column of \tilde{Y} is the transpose of the kinetic order matrix row of the complex's reaction, otherwise (i.e., for non-reactant complexes), the column is 0. We form the **T-matrix** of a PL-RDK system by truncating away the columns of the non-reactant complexes in \tilde{Y} , obtaining an $m \times n_r$ matrix.

Arceo et al. [2] investigated the relationship between the reactant subspace of a system and its kinetic behavior. They identified a class of networks, called RSS network, to be particularly interesting. A CRN has the **RSS (reactant-determined stoichiometric subspace) property** (or type RSS) if S is contained in R . Moreover, Arceo et al. introduced the notion of kinetic flux subspace \tilde{S} of a PL-RDK system on an RSS network. For a PL-RDK system on an RSS network, the **kinetic flux subspace** \tilde{S} is the subspace $T(Y_{\text{res}}^{-1}(S))$.

Talabis et al. [18] identified some subsets of PL-RDK systems, one of which is the PL-RLK systems.

Definition 9. A chemical kinetics K is said to be **reactant set linear independent** (of type **PL-RLK**) if the columns of T are linearly independent.

The Deficiency Zero Theorem of Talabis et al. applies for a set of kinetics called PL-TIK and PL-TLK systems. A chemical kinetics is considered to be any of these type if the so-called *augmented T-matrix* of the system (see [18]) is column maximal. Nevertheless, it was shown in the study that a PL-TIK system with a single linkage class and with no inflow reactions (that is, there are no reactions having zero reactant complex) is a PL-RLK system. We can, thus, restate (the first two statements of) the DZT for PL-TIK of Talabis et al. [18] as:

Theorem 1 (Deficiency Zero Theorem for PL-RLK Systems). *Let (\mathcal{N}, K) be a PL-RLK system with $\ell = 1$ and $\delta = 0$. Then*

(i) $E_+(\mathcal{N}, K) \neq \emptyset$ if and only if \mathcal{N} is strongly connected, and

(ii) if $E_+(\mathcal{N}, K) \neq \emptyset$ and $x^* \in E_+(\mathcal{N}, K)$, then

$$E_+(\mathcal{N}, K) = \{x \in \mathbb{R}_{>0}^{\mathcal{J}} \mid \log x - \log x^* \in \tilde{S}^\perp\}. \quad (2.4)$$

Finally, we briefly review some notions related to decomposition of chemical kinetic systems.

Definition 10. A **subnetwork** $\mathcal{N}' = (\mathcal{S}', \mathcal{C}', \mathcal{R}')$ of a chemical reaction network $\mathcal{N} = (\mathcal{S}, \mathcal{C}, \mathcal{R})$ is the sub-digraph defined by a subset $\mathcal{R}' \subset \mathcal{R}$, i.e. \mathcal{C}' is the subset of complexes occurring in \mathcal{R}' , and \mathcal{S}' is the subset of species occurring in \mathcal{C}' . The **embedded representation** of a subnetwork \mathcal{N}' is the triple $(\mathcal{S}', \mathcal{C}', \mathcal{R}')$. A set of subnetworks $\{\mathcal{N}_i = (\mathcal{S}_i, \mathcal{C}_i, \mathcal{R}_i), i = 1, \dots, k\}$ is a **network decomposition** of $\mathcal{N} = (\mathcal{S}, \mathcal{C}, \mathcal{R})$ if $\{\mathcal{R}_i\}$ forms a partition of \mathcal{R} .

Feinberg introduced the important concept of independence in his review:

Definition 11. A network decomposition is **independent** if $S = S_1 + S_2 + \dots + S_k$ is direct. A subnetwork $\mathcal{N}' = (\mathcal{S}', \mathcal{C}', \mathcal{R}')$ is called independent if the decomposition induced by $\{\mathcal{R}', \mathcal{R} \setminus \mathcal{R}'\}$ is independent.

Proposition 1. *A network decomposition is independent if and only if $s = s_1 + s_2 + \dots + s_k$. Every subnetwork in an independent decomposition is an independent subnetwork.*

Arceo et al. [1] introduced a semigroup structure on the set of kinetics on \mathcal{N} via componentwise multiplication, for any network $\mathcal{N} = (\mathcal{S}, \mathcal{C}, \mathcal{R})$. If $P(\mathcal{R}) = \{\mathcal{R}_1, \mathcal{R}_2, \dots, \mathcal{R}_k\}$ is a partition of \mathcal{R} , then for any kinetics K on \mathcal{N} , we have the **kinetic factor** K_i of K on \mathcal{R}_i to be the kinetics $K_i : \mathbb{R}^{\mathcal{J}} \rightarrow \mathbb{R}^{\mathcal{R}}$ with $K_{i,r}(x) = K_r(x)$ if $r \in \mathcal{R}_i$, and 1 otherwise.

Definition 12. A decomposition of the chemical kinetic system (\mathcal{N}, K) consists of the network decomposition $\mathcal{N} = \mathcal{N}_1 + \mathcal{N}_2 + \dots + \mathcal{N}_k$ and kinetics factorization $K = K_1 K_2 \dots K_k$ generated by a partition $P(\mathcal{R}) = \{\mathcal{R}_1, \mathcal{R}_2, \dots, \mathcal{R}_k\}$. We will denote the CKS decompositions with $(\mathcal{N}, K) = (\mathcal{N}_1, K_1) + (\mathcal{N}_2, K_2) + \dots + (\mathcal{N}_k, K_k)$.

On the level of the species formation rate function, a network decomposition induces the formation of partial sums, i.e. $f = f_1 + f_2 + \dots + f_k$, where $f_i = N_i K_i$, where $(N_i)_{u,v} = N_{u,v}$ for $v \in \mathcal{R}_i$, and 0 otherwise. Equivalently, $f_i(x)$ is the partial sum consisting of summands $K_i(x)(y'_i - y_i)$ for reactions $y_i \rightarrow y'_i \in \mathcal{R}_i$. For any subnetwork of a decomposition, we define $E_+(\mathcal{N}_i, K_i)$ to be the **set of positive equilibria of its embedded representation** $(\mathcal{S}_i, \mathcal{C}_i, \mathcal{R}_i)$, i.e. the set $\{x \in \mathbb{R}_{>0}^{\mathcal{S}} | f_i(x) = 0\}$.

Feinberg [6] established the relationship between the positive equilibria of the “parent network” and those of the subnetworks of a decomposition in the following result.

Theorem 2 (Feinberg Decomposition Theorem, [6]). *Let $P(\mathcal{R}) = \{\mathcal{R}_1, \mathcal{R}_2, \dots, \mathcal{R}_k\}$ be a partition of a CRN \mathcal{N} and let K be a kinetics on \mathcal{N} . If $\mathcal{N} = \mathcal{N}_1 + \mathcal{N}_2 + \dots + \mathcal{N}_k$ is the network decomposition of $P(\mathcal{R})$ and $E_+(\mathcal{N}_i, K_i) = \{x \in \mathbb{R}_{>0}^{\mathcal{S}} | N_i K_i(x) = 0\}$, then*

- (i) $E_+(\mathcal{N}_1, K_1) \cap E_+(\mathcal{N}_2, K_2) \cap \dots \cap E_+(\mathcal{N}_k, K_k) \subseteq E_+(\mathcal{N}, K)$.
- (ii) *If the network decomposition is independent, then equality holds.*

For reference, we consider a special network decomposition:

Definition 13. A network decomposition $\mathcal{N} = \mathcal{N}' + \mathcal{N}''$ is said to be **trivial** if \mathcal{N}' is a subnetwork whose stoichiometric subspace coincides with that of the whole network.

This allows us to interpret the following Joshi-Shiu Equilibria Lifting Theorem [11] as a result about a trivial decomposition of a network:

Theorem 3 (Joshi-Shiu Equilibrium Lifting Theorem, [11]). *Let \mathcal{N} be a subnetwork of a chemical reaction network \mathcal{G} such that they have the same stoichiometric subspace: $S_{\mathcal{N}} = S_{\mathcal{G}}$. Let \mathcal{K} be a parametrized family of kinetics on the species of \mathcal{G} . Then if \mathcal{N} admits multiple nondegenerate positive \mathcal{K} steady states, then \mathcal{G} does as well. Additionally, if \mathcal{N} admits finitely many such steady states, then \mathcal{G} admits at least as many.*

Remark 3. Arceo et al. [3] showed that in the context of power-law kinetics, the set of parametrized family of kinetics points to the power-law kinetic system with non-negative kinetic orders.

3 Main Result

3.1 A Deficiency Zero Theorem Beyond PL-RDK Systems

As a requirement to prove our main result, we state the following basic result, which has not been documented in the CRNT literature:

Lemma 1. *If a network has independent decomposition $\mathcal{N} = \mathcal{N}_1 + \mathcal{N}_2 + \cdots + \mathcal{N}_k$, then $\delta \leq \delta_1 + \delta_2 + \cdots + \delta_k$.*

This is a generalization of the well-known fact, that if the decomposition is the linkage class decomposition, independence implies $\delta = \delta_1 + \delta_2 + \cdots + \delta_k$.

Proof. If \mathcal{R}_i is the reaction set of \mathcal{N}_i , we claim that

$$\text{Im } I_a = \text{Im } I_{a,1} + \text{Im } I_{a,2} + \cdots + \text{Im } I_{a,k}, \quad (3.1)$$

where $I_{a,i}$ is the restriction of I_a to the subspace $\mathbb{R}^{\mathcal{R}_i}$. Clearly, each of the summands on the RHS of Equation (3.1) is contained in $\text{Im } I_a$. On the other hand, any element of $\text{Im } I_a$ is of the form $\sum \alpha_j I_a(\omega_{r_j})$ with $r_j \in \mathcal{R}$. Since the \mathcal{R}_i 's partition \mathcal{R} , we can group the summands to partial sums with reactions in \mathcal{R}_i , and these partial sums are in $\text{Im } I_{a,i}$. From Linear Algebra, we have

$$n - \ell = \dim(\text{Im } I_a) \leq \sum_{i=1}^k \dim(\text{Im } I_{a,i}) = \sum_{i=1}^k (n_i - \ell_i). \quad (3.2)$$

Subtracting s from the LHS of Equation (3.2) and $s_1 + s_2 + \cdots + s_k$ from the RHS (the subtrahends are equal due to decomposition independence; see Proposition 1), we obtain the desired result. ■

By definition, if the decomposition of a network is independent, we cannot find a nonzero vector in the intersection of the resulting stoichiometric subspaces of the subnetworks. The following result asserts that the same property can be observed among the kinetic flux subspaces of the weakly reversible subnetworks generated by independent decomposition of PL-RLK systems with zero reactant deficiency.

Lemma 2. *Let $\mathcal{N} = \mathcal{N}_1 + \mathcal{N}_2 + \cdots + \mathcal{N}_k$ be an independent decomposition and K a kinetics with factorization $K = K_1 K_2 \cdots K_k$. If the subnetworks are weakly reversible with zero reactant deficiency and K_i 's are in PL-RLK, then $\tilde{S}_1 \cap \tilde{S}_2 \cap \cdots \cap \tilde{S}_k = \{0\}$.*

Proof. Since the subnetworks are all weakly reversible (each reaction is in a cycle), the whole network is also weakly reversible, so that T and Y_{res}^{-1} are well defined. The restrictions of T and Y_{res}^{-1} to each \mathcal{N}_i yields an isomorphisms between the kinetic flux and stoichiometric subspaces. If a non-zero x , say is in $\tilde{S}_1 \cap \tilde{S}_2$, then $Y_{\text{res}}(T^{-1}(x))$ would be a non-zero element in $S_1 \cap S_2$, a contradiction to the independence of the decomposition.

■

We now state and prove our main result. The theorem includes a statement about the existence of positive equilibria. The proof of this statement is adapted from Feinberg's derivation of the Lemma 8.2.1 in [7]. Our theorem also includes a statement about the parametrization of the set of positive equilibria, which is derived directly from the DZT for PL-TIK of Talabis et al. [18]. Unlike the DZT for mass-action systems, we do not formulate a uniqueness statement in each stoichiometric class since this would also depend on the latter, and would contain only statements with respect to the kinetic classes, and not the stoichiometric classes. Moreover, in contrast to the previous DZTs, the weak reversibility and zero deficiency of the network need not be explicitly assumed since these properties follow from those of the independent decomposition.

Theorem 4. *If a PLK system (\mathcal{N}, K) has an independent decomposition into weakly reversible subnetworks $\mathcal{N}_1, \mathcal{N}_2, \dots, \mathcal{N}_k$ with zero reactant deficiency and PL-RLK kinetics K_1, K_2, \dots, K_k , then*

- (i) \mathcal{N} is a weakly reversible network with $\delta = 0$;
- (ii) $E_+(\mathcal{N}, K) \neq \emptyset$; and
- (iii) If x^* is a positive equilibrium, then

$$E_+(\mathcal{N}, K) = \{x \in \mathbb{R}_{>0}^{\mathcal{S}} \mid \log x - \log x^* \in (\tilde{S}_1 + \tilde{S}_2 + \dots + \tilde{S}_k)^\perp\}. \quad (3.3)$$

Proof. Since each subnetwork is weakly reversible, every reaction in a subnetwork must be in a cycle. Moreover, since the subnetwork reaction sets partition the network's reaction set, the entire network must be weakly reversible. Since on weakly reversible networks, $\delta_\rho \geq \delta$ (see Remark 1), each subnetwork has zero deficiency. By Lemma 1, the network has zero deficiency. To prove (ii) and (iii), we consider the case where $k = 2$. By the first statement of Theorem 1 (DZT for PL-RLK),

$$E_+(\mathcal{N}_1, K_1) \neq \emptyset \text{ and } E_+(\mathcal{N}_2, K_2) \neq \emptyset.$$

Moreover, if $x_1 \in E_+(\mathcal{A}_1, K_1)$ and $x_2 \in E_+(\mathcal{A}_2, K_2)$, then

$$E_+(\mathcal{A}_1, K_1) = \{x \in \mathbb{R}^{\mathcal{S}} \mid \log x - \log x_1 \in (\tilde{S}_1)^\perp\}, \text{ and}$$

$$E_+(\mathcal{A}_2, K_2) = \{x \in \mathbb{R}^{\mathcal{S}} \mid \log x - \log x_2 \in (\tilde{S}_2)^\perp\}.$$

Since the decomposition is independent, by Theorem 2 (Feinberg Decomposition Theory),

$$E_+(\mathcal{A}, K) = E_+(\mathcal{A}_1, K_1) \cap E_+(\mathcal{A}_2, K_2).$$

Thus, to show that the whole network admits positive equilibria, we must show that $E_+(\mathcal{A}_1, K_1) \cap E_+(\mathcal{A}_2, K_2)$ is non-empty. That is, $x^* \in E_+(\mathcal{A}, K)$ if and only if $x^* \in E_+(\mathcal{A}_1, K_1) \cap E_+(\mathcal{A}_2, K_2)$. Equivalently,

$$\log x^* \in [\log x_1 + (\tilde{S}_1)^\perp] \cap [\log x_2 + (\tilde{S}_2)^\perp].$$

That $[\log x_1 + (\tilde{S}_1)^\perp] \cap [\log x_2 + (\tilde{S}_2)^\perp]$ is non-empty follows from the following result involving cosets:

$$[\log x_1 + (\tilde{S}_1)^\perp] \cap [\log x_2 + (\tilde{S}_2)^\perp] \neq \emptyset \quad \text{if and only if} \quad \log x_1 - \log x_2 \in (\tilde{S}_1)^\perp + (\tilde{S}_2)^\perp. \quad (3.4)$$

Statement (3.4) can be proven easily and straightforwardly from the definition of a left coset (see [8] to recall the definition of a left coset). From Lemma 2, we have $\tilde{S}_1 \cap \tilde{S}_2 = \{0\}$. Hence,

$$(\tilde{S}_1)^\perp + (\tilde{S}_2)^\perp = (\tilde{S}_1 \cap \tilde{S}_2)^\perp = \{0\}^\perp = \mathbb{R}^{\mathcal{S}}.$$

Clearly, $\log x_1 - \log x_2 \in \mathbb{R}^{\mathcal{S}}$ and so, $[\log x_1 + (\tilde{S}_1)^\perp] \cap [\log x_2 + (\tilde{S}_2)^\perp] \neq \emptyset$. Let

$$w \in [\log x_1 + (\tilde{S}_1)^\perp] \cap [\log x_2 + (\tilde{S}_2)^\perp],$$

and take $x^* := e^w$. Since $w \in \log x_1 + (\tilde{S}_1)^\perp$, we can see that $x^* \in E_+(\mathcal{A}_1, K_1)$. Similarly, $x^* \in E_+(\mathcal{A}_2, K_2)$. Therefore, $x^* \in E_+(\mathcal{A}, K)$. From Algebra (see [14]), we have $[(\tilde{S}_1)^\perp \cap (\tilde{S}_2)^\perp] = (\tilde{S}_1 + \tilde{S}_2)^\perp$. Hence,

$$[\log x_1 + (\tilde{S}_1)^\perp] \cap [\log x_2 + (\tilde{S}_2)^\perp] = \log x^* + [(\tilde{S}_1)^\perp \cap (\tilde{S}_2)^\perp] = \log x^* + (\tilde{S}_1 + \tilde{S}_2)^\perp.$$

It follows that

$$\left\{ x \in \mathbb{R}^{\mathcal{S}} \mid \log x - \log x^* \in (\tilde{S}_1 + \tilde{S}_2)^\perp \right\} = E_+(\mathcal{A}_1, K_1) \cap E_+(\mathcal{A}_2, K_2) = E_+(\mathcal{A}, K).$$

An inductive argument can be carried out to prove for the general case. ■

3.2 Application to a Carbon Cycle Model

The Earth system of Schmitz [15] is a simple mass balance model which accounts for the movement of carbon among different pools that represent major parts of the Earth. In the pre-industrial state, six major carbon pools are considered. Figure 1 provides a schematic diagram of the model. The state variables M_i , in petagrams of carbon (PgC), stand for the mass of carbon in the pool at time t . The arrows represent the transfer of carbon, in petagrams of carbon per year (PgC/y), among the different carbon pools. These arrows are labelled by their fluxes F_{ij} , which indicates the rate of transfer of carbon from M_i to M_j . A detailed motivation of the model design and underlying assumptions are given in [15].

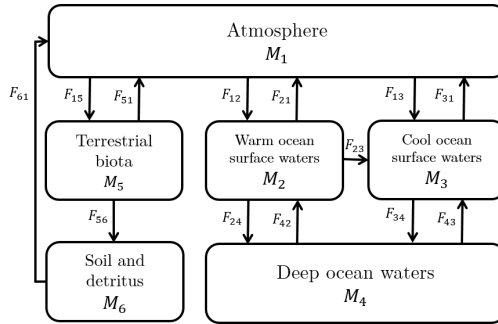


Figure 1. Schematic diagram of Schmitz’s carbon cycle model at pre-industrial state [15].

The transfer functions provided by Schmitz are all power-law functions (the majority being mass-action kinetics) with the exception of F_{15} . We constructed a power-law approximation of the exception using a standard method from Biochemical Systems Theory (BST) to obtain a Generalized Mass Action (GMA) system, i.e. a system with only power law rate functions. More precisely, GMA system is a modelling format, based on ordinary differential equations (ODEs), wherein every mass transfer rate is approximated separately with a power-law term, and these terms are added together, with a plus sign for incoming fluxes and a minus sign for outgoing fluxes [21, 22]. The aforementioned approximation method is based on Taylor approximation in logarithmic coordinates. By applying such approach, the function F_{15} results to a power-law function of M_1 , i.e. $F_{15} = k'_{15} M_1^{0.36}$, where k'_{15} is a rate constant. The resulting GMA system is provided in Equation (3.5).

$$\left. \begin{aligned}
 \dot{M}_1 &= k_{21}M_2^{9.4} + k_{31}M_3^{10.2} + k_{51}M_5 + k_{61}M_6 - k_{12}M_1 - k_{13}M_1 - k'_{15}M_1^{0.36} \\
 \dot{M}_2 &= k_{12}M_1 + k_{42}M_4 - k_{23}M_2 - k_{24}M_2 - k_{21}M_2^{9.4} \\
 \dot{M}_3 &= k_{13}M_1 + k_{23}M_2 + k_{43}M_4 - k_{34}M_3 - k_{31}M_3^{10.2} \\
 \dot{M}_4 &= k_{24}M_2 + k_{34}M_3 - k_{42}M_4 - k_{43}M_4 \\
 \dot{M}_5 &= k'_{15}M_1^{0.36} - k_{51}M_5 - k_{56}M_5 \\
 \dot{M}_6 &= k_{56}M_5 - k_{61}M_6
 \end{aligned} \right\} \quad (3.5)$$

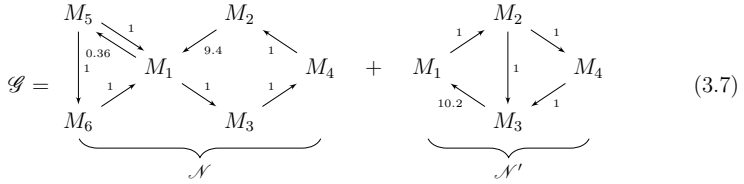
Instead of confronting this GMA system, we identify the kind of dynamics that this system admits by analyzing its dynamically equivalent CRN representation. By **dynamic equivalence**, we mean that the two systems – the GMA system and the CRN representation– both have the same set of differential equations [3]. The procedure to obtain a dynamically equivalent CRN representation for any GMA system can be found in [3]. Particularly, the GMA system in (3.5) is dynamically equivalent to the CRN in (1.1) (on page 3) with associated power-law kinetics encoded in the following kinetic order matrix:

$$F = \begin{array}{cccccc} & M_1 & M_2 & M_3 & M_4 & M_5 & M_6 \\ \left[\begin{array}{cccccc} 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0.36 & 0 & 0 & 0 & 0 & 0 \\ 0 & 9.4 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 10.2 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right] & \begin{array}{l} M_1 \rightarrow M_2 \\ M_1 \rightarrow M_3 \\ M_1 \rightarrow M_5 \\ M_2 \rightarrow M_1 \\ M_2 \rightarrow M_3 \\ M_2 \rightarrow M_4 \\ M_3 \rightarrow M_1 \\ M_3 \rightarrow M_4 \\ M_4 \rightarrow M_2 \\ M_4 \rightarrow M_3 \\ M_5 \rightarrow M_1 \\ M_5 \rightarrow M_6 \\ M_6 \rightarrow M_1 \end{array} \end{array} \quad (3.6)$$

To verify their dynamic equivalence, one may apply Equations (2.1) and (2.2) to see that the SFRF of the CRN representation is, in fact, similar to the ODE system in (3.5).

The analysis of the system’s CRN representation and associated power-law kinetics allows us to use tools from CRNT, particularly its deficiency-oriented analysis. Consider now the following trivial decomposition (see Definition 13) $\mathcal{G} = \mathcal{N} + \mathcal{N}'$ of the whole

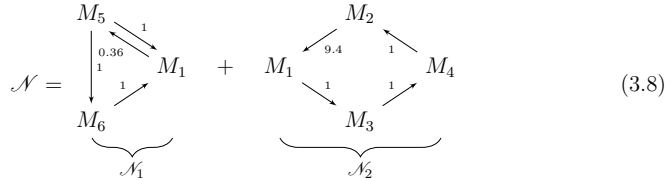
network:



Note that in (3.7) the arrow labels refer to the kinetic orders. Observe that the subnetwork \mathcal{N} of the whole CRN is weakly reversible with $\delta = 0$, and whose kinetic system is of type PL-NDK. Furthermore, an independent decomposition of \mathcal{N} can be found by partitioning its reactions into two sets

$$\begin{aligned} \mathcal{R}_1 &= \{M_1 \rightarrow M_5, M_5 \rightarrow M_1, M_5 \rightarrow M_6, M_6 \rightarrow M_1\} \text{ and} \\ \mathcal{R}_2 &= \{M_1 \rightarrow M_3, M_3 \rightarrow M_4, M_4 \rightarrow M_2, M_2 \rightarrow M_1\}. \end{aligned}$$

This results to two zero reactant-deficiency PL-RLK subnetworks, \mathcal{N}_1 and \mathcal{N}_2 :



By Theorem 4, $E_+(\mathcal{N}, K)$ is non-empty. Furthermore, if $x^* \in E_+(\mathcal{N}, K)$, then

$$E_+(\mathcal{N}, K) = \left\{ x \in \mathbb{R}^{\mathcal{S}} \mid \log x - \log x^* \in \left(\tilde{\mathcal{S}}_1 + \tilde{\mathcal{S}}_2 \right)^\perp \right\}, \quad (3.9)$$

where

$$\left(\tilde{\mathcal{S}}_1 + \tilde{\mathcal{S}}_2 \right)^\perp = \tilde{\mathcal{S}}_1^\perp \cap \tilde{\mathcal{S}}_2^\perp = \left\langle [1, 0.1064, 1, 1, 0.36, 0.36]^\top \right\rangle.$$

Finally, to show that a positive steady state for the entire network \mathcal{G} exists, we appeal to the Joshi-Shiu Equilibrium Lifting Theorem (Theorem 3). It remains show that equilibrium points $E_+(\mathcal{N}, K)$ are non-degenerate. Computations show that

$$E_+(\mathcal{N}, K) = \left\langle \left[M_1, \left(\frac{k_{13}}{k_{21}} M_1 \right)^{9.4^{-1}}, \frac{k_{13}}{k_{34}} M_1, \frac{k_{13}}{k_{42}} M_1, \frac{k'_{15}}{k_{51} + k_{56}} M_1^{0.36}, \frac{k'_{15} k_{56}}{k_{61} (k_{51} + k_{56})} M_1^{0.36} \right]^\top \right\rangle. \quad (3.10)$$

Suppose f is the species formation rate function associated with \mathcal{N} , and let $x^* \in$

$E_+(\mathcal{N}, K)$. The Jacobian matrix of f at x^* is computed to be

$$J_{x^*}(f) = \begin{bmatrix} -k_{13} - pk'_{15}M_1^{p-1} & \beta k_{21}M_2^{\beta-1} & 0 & 0 & k_{51} & k_{61} \\ 0 & -\beta k_{21}M_2^{\beta-1} & 0 & k_{42} & 0 & 0 \\ k_{13} & 0 & -k_{34} & 0 & 0 & 0 \\ 0 & 0 & k_{34} & -k_{42} & 0 & 0 \\ pk'_{15}M_1^{p-1} & 0 & 0 & 0 & -(k_{51} + k_{56}) & 0 \\ 0 & 0 & 0 & 0 & k_{56} & -k_{61} \end{bmatrix}, \quad (3.11)$$

with $\beta = 9.4$ and $p = 0.36$. It can be verified that $\text{Ker } J_{x^*}(f) \cap S = \{0\}$, where S is the stoichiometric subspace of \mathcal{N} . Hence, \mathcal{N} has non-degenerate set of positive equilibrium points. Furthermore, the entire network \mathcal{G} corresponding to the CRN representation of the power-law approximation of the pre-industrial carbon cycle of Schmitz admits positive equilibria. In fact, \mathcal{G} has at least as many non-degenerate positive equilibria as its subnetwork \mathcal{N} .

4 Conclusion and Outlook

In conclusion, we summarize our results and outline some perspectives for further research.

1. We presented an extension of the well-known characterization of independent linkage class decomposition $\delta = \delta_1 + \delta_2 + \dots + \delta_\ell$ to an inequality $\delta \leq \delta_1 + \delta_2 + \dots + \delta_k$ for an independent decomposition.
2. Our main result is the first Deficiency Zero Theorem that is valid for a class of kinetics with non-reactant determined kinetic orders. The theorem includes statements about the existence of positive equilibria of the system and the parametrization of the set of positive equilibria. However, there is no general uniqueness statement with respect to a stoichiometric class. Unlike previous DZTs, the weak reversibility and zero deficiency of the network may not be explicitly assumed since these properties follow from those of the independent decomposition.
3. We applied the results to characterize the positive equilibria of a power law approximation of R. Schmitz's model of the Earth's carbon cycle in its pre-industrial state.

The application of other decomposition schemes for the inference of positive equilibria for the corresponding chemical kinetic systems is a promising area of study. Moreover, exploring the extension of CRN decomposition to incorporate concepts such as modularity

widely used in the Theory of Complex Networks and Systems Biology offers a further interesting research perspective.

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