Conservation-dissipation structure of chemical reaction systems

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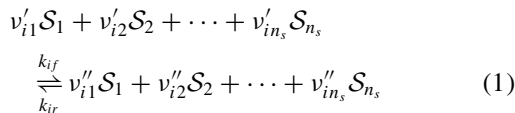(Received 31 August 2012; published 5 December 2012)

In this Brief Report, we show that balanced chemical reaction systems governed by the law of mass action have an elegant conservation-dissipation structure. From this structure a number of important conclusions can be easily deduced. In particular, with the help of this structure we can rigorously justify the classical partial equilibrium approximation in chemical kinetics.

Chemical reactions are fundamental for many natural phenomena, ranging from the rusting of iron to cell cycling and from photosynthesis to apoptosis. Since J. Wei [1] proposed a set of axioms to characterize general chemical systems in 1962, there have been huge efforts in seeking a unified mathematical formulation of chemical reactions. Oster and Perelson [2], for example, presented a geometric structure by casting much of the classical theory of kinetics into the language of differential geometry in 1974. Very recently in Ref. [3] van der Schaft *et al.* derived a general graph-theoretic formulation, which is basically already contained in the innovative paper by Sontag [4]. Other general studies of the mathematical structure of chemical systems include those of Aris [5–7], Bowen [8,9], Coleman and Gurtin [10], Feinberg [11–13], Horn [14], Horn and Jackson [15], Krambeck [16], Sellers [17], Shapiro and Shapley [18], Wei [19], Wei and Prater [20], and so on. See Refs. [21,22] for more references.

In this report, we present a conservation-dissipation structure of the chemical reaction equations. It will be seen that this new structure is different from all those mentioned above. Consider a reaction system with n_s species participating in n_r reversible reactions

$$v'_{i1}\mathcal{S}_1 + v'_{i2}\mathcal{S}_2 + \cdots + v'_{in_s}\mathcal{S}_{n_s}$$
$$\underset{k_{ir}}{\overset{k_{if}}{\rightleftharpoons}} v''_{i1}\mathcal{S}_1 + v''_{i2}\mathcal{S}_2 + \cdots + v''_{in_s}\mathcal{S}_{n_s} \quad (1)$$

for $i = 1, 2, \ldots, n_r$. Here $\mathcal{S}_k$ is the chemical symbol for the kth species, the nonnegative integers v'_{ik} and v''_{ik} are the stoichiometric coefficients of the kth species in the ith reaction, and k_{if} and k_{ir} are the respective direct and reverse constants of the ith reaction. The reversibility means that both k_{if} and k_{ir} are positive.

Denote by u_k the concentration of the kth species $\mathcal{S}_k$. According to the law of mass action, the evolution of $u_k = u_k(t)$ obeys the ordinary differential equations (see, e.g., Ref. [22]):

$$\frac{du_k}{dt} = \sum_{i=1}^{n_r}(v''_{ik} - v'_{ik})\left(k_{if}\prod_{j=1}^{n_s}u_j^{v'_{ij}} - k_{ir}\prod_{j=1}^{n_s}u_j^{v''_{ij}}\right). \quad (2)$$

Set $u = (u_1, u_2, \ldots, u_{n_s})^T$ with the superscript T for the transpose. The free energy of the reaction system is defined as

$$F(u) = \sum_{k=1}^{n_s}(u_k \ln u_k - u_k \ln u_k^* - u_k)$$

with $u^* = (u_1^*, u_2^*, \ldots, u_{n_s}^*)^T$ a constant state to be specified below. Clearly, the gradient of $F = F(u)$ is

$$\frac{\partial F}{\partial u} = \left(\ln u_1 - \ln u_1^*, \ln u_2 - \ln u_2^*, \ldots, \ln u_{n_s} - \ln u_{n_s}^*\right)^T \quad (3)$$

and $F(u)$ is convex with respect to u.

The aforesaid conservation-dissipation structure is given in the following theorem, which will be proved at the end of this report.

Theorem. Assume that the system described by Eq. (2) satisfies the principle of detailed balance: there are n_s positive numbers, $u_i^* > 0$, such that

$$k_{if}\prod_{j=1}^{n_s}(u_j^*)^{v'_{ij}} = k_{ir}\prod_{j=1}^{n_s}(u_j^*)^{v''_{ij}} \quad (4)$$

for $i = 1, 2, \ldots, n_r$. Then there is a symmetric and nonpositive definite matrix, $S = S(u)$, defined for u with $u_i > 0 (i = 1, 2, \ldots, n_s)$, such that the kinetic Eq. (2) can be rewritten as

$$\frac{du}{dt} = S(u)\frac{\partial F}{\partial u} \quad (5)$$

and the null space of $S(u)$ is

$$\text{span}\left\{\left(v''_{i1} - v'_{i1}, v''_{i2} - v'_{i2}, \ldots, v''_{in_s} - v'_{in_s}\right)^T, i = 1, 2, \ldots, n_r\right\}^\perp,$$

which is independent of u with $u_i > 0 (i = 1, 2, \ldots, n_s)$.

Remark that the constant state $u^* = (u_1^*, u_2^*, \ldots, u_{n_s}^*)^T$ needs not be unique and is often not unique. The symmetry of $S(u)$ is reminiscent of the celebrated Onsager reciprocal relation [23], but it is different from that due to the dependence of $S(u)$ on u. The null space of $S(u)$ is just the right null space of the $n_r \times n_s$-stoichiometric matrix

$$\begin{pmatrix} v''_{11} - v'_{11} & v''_{12} - v'_{12} & \cdots & v''_{1n_s} - v'_{1n_s} \\ v''_{21} - v'_{21} & v''_{22} - v'_{22} & \cdots & v''_{2n_s} - v'_{2n_s} \\ \vdots & \vdots & \vdots & \vdots \\ v''_{n_r1} - v'_{n_r1} & v''_{n_r2} - v'_{n_r2} & \cdots & v''_{n_rn_s} - v'_{n_rn_s} \end{pmatrix}$$

and is just the orthogonal complement of the stoichiometric subspace [13]. Its independence on u has a clear physical

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interpretation (see below) and seems crucial mathematically [24]. We also notice that the null space contains nontrivial vectors. In fact, let n_e be the number of elements involved in the system and denote by e_{kl} the number of the lth element in the kth species. We have the element conservation relations

$$\sum_k v'_{ik} e_{kl} = \sum_k v''_{ik} e_{kl} \qquad (6)$$

for $i = 1, 2, \ldots, n_r$ and $l = 1, 2, \ldots, n_e$. Namely,

$$(e_{1l}, e_{2l}, \ldots, e_{n_s l}) \perp \left(v''_{i1} - v'_{i1}, v''_{i2} - v'_{i2}, \ldots, v''_{in_s} - v'_{in_s} \right)$$

for $i = 1, 2, \ldots, n_r$ and $l = 1, 2, \ldots, n_e$. Thus, the n_e vectors $(e_{1l}, e_{2l}, \ldots, e_{n_s l})$ are all in the null space of $S(u)$.

Next, we deduce some important consequences from the above theorem. For each constant vector v in the null space, we have

$$\frac{d[v^T u(t)]}{dt} = v^T S(u) \frac{\partial F}{\partial u} \equiv 0.$$

Therefore, $v^T u(t)$ is a conservative quantity. Because the null space is not empty, we have simply shown the existence of such conserved quantities. This is a well-known fact. In the language of Feinberg and collaborators [13], this is equivalent to saying that there are distinct stoichiometric compatibility classes that are invariant of the dynamics. On the other hand, the u-independence of the null space simply reflects the fact that the physical laws of conservation hold true no matter what the state of the system is in. Moreover, since $S(u)$ is symmetric and nonpositive definite, it is immediate to see the well-known fact

$$\frac{dF(u(t))}{dt} = \left(\frac{\partial F}{\partial u} \right)^T \frac{du(t)}{dt} = \left(\frac{\partial F}{\partial u} \right)^T S(u) \frac{\partial F}{\partial u} \leqslant 0.$$

Namely, $F(u)$ is a Lyapunov function for the reaction system (5). Because $S(u)$ is not equal to the identical matrix, the decease of $F(u(t))$ does not follow the steepest descending path, generally, which was observed in Ref. [25].

In view of Öttinger's general equation for nonequilibrium reversible-irreversible coupling (GENERIC) framework [26], our theorem indicates that the chemical reaction system with detailed balance falls into the GENERIC framework, with an irreversible part only but without any reversible part. In contrast, the Hamiltonian mechanics [27] was regarded in Ref. [26] as a typical example in the framework, with a reversible part only but without any irreversible part. Let us mention that there seems to be no discussion on the u-independence of the null space of the friction matrix in Ref. [26].

As an application of our theorem, we show the validity of the classical partial equilibrium approximation (PEA) method for model reduction in chemical kinetics (see, e.g., Ref. [28]). For this purpose, we consider a chemical reaction system (closed or open), containing the reactions in Eq. (1) as fast. In this situation, the kinetics can be written as

$$\frac{du_k}{dt} = \frac{1}{\varepsilon} \sum_{i=1}^{n_r} (v''_{ik} - v'_{ik}) \left(k_{if} \prod_{j=1}^{n_s} u_j^{v'_{ij}} - k_{ir} \prod_{j=1}^{n_s} u_j^{v''_{ij}} \right) + p_k(u),$$

$$(7)$$

where $\varepsilon > 0$ is a small parameter characterizing the fastness and $p_k(u)$ stands for the contributions due to the slow reactions. With the PEA method, this system of equations (7) can be simplified by letting the fast part vanish, that is,

$$\sum_{i=1}^{n_r} (v''_{ik} - v'_{ik}) \left(k_{if} \prod_{j=1}^{n_s} u_j^{v'_{ij}} - k_{ir} \prod_{j=1}^{n_s} u_j^{v''_{ij}} \right) = 0. \qquad (8)$$

Indeed, from these n_s nonlinear equations fast modes of u may be algebraically expressed in terms of slow ones [24] and the latter solve a system of ordinary differential equations. Because the number of the latter is less than n_s, the two-scale system (7) is simplified.

Now we show the reasonableness of this simplification process by using the above theorem and the singular perturbation theory [29]. If the principle of detailed balance is verified for the fast part only, Eq. (7) can be rewritten as

$$\frac{du}{dt} = \frac{1}{\varepsilon} S(u) \frac{\partial F}{\partial u} + \left[p_1(u), p_2(u), \ldots, p_{n_s}(u) \right]^T. \qquad (9)$$

In order to apply the singular perturbation theory to this two-scale system, we compute the Jacobian of the fast part at a state u_e, satisfying $S(u_e) \frac{\partial F}{\partial u}(u_e) = 0$, which needs not be u^*:

$$\frac{\partial}{\partial u} \left[S(u) \frac{\partial F}{\partial u} \right] \bigg|_{u=u_e} = S(u_e) \frac{\partial^2 F}{\partial u \partial u}(u_e) + \frac{\partial}{\partial u} \left[S(u) \frac{\partial F}{\partial u}(u_e) \right] \bigg|_{u=u_e}$$

$$= S(u_e) \frac{\partial^2 F}{\partial u \partial u}(u_e).$$

For the second equality we have used that $S(u_e) \frac{\partial F}{\partial u}(u_e) = 0$. In fact, by the definition $\frac{\partial F}{\partial u}(u_e)$ is in the null space of $S(u_e)$ and, thereby, in the null space of $S(u)$, for the null space of $S(u)$ is the same as that of $S(u_e)$. Therefore, we have $S(u) \frac{\partial F}{\partial u}(u_e) \equiv 0$. Since $F(u)$ is strictly convex, its Hessian $F_{uu}(u_e)$ is positive-definite. Recall that $S(u)$ is symmetric and nonpositive definite. It is elementary that the Jacobian matrix $S(u_e) F_{uu}(u_e)$ is similar to a real diagonal matrix with nonpositive elements. Thus, we have verified the stability condition in Ref. [29] (see also Ref. [24]). According to the singular perturbation theory, the solution to an initial-value problem of the two-scale system (9) uniformly converges, in any bounded-time interval away from $t = 0$, as ε goes to zero and the limit solves the algebraic Eq. (8) and the corresponding simplified system. In this way, we have justified the classical PEA method.

The main points of this report are summarized in the abstract. We conclude our discussion with a complete proof of the theorem.

Proof. Since k_{if}, k_{ir} and u_i^* are all positive, we see that

$$\ln k_{if} - \ln k_{ir} = -\sum_{j=1}^{n_s} (v'_{ij} - v''_{ij}) \ln u_j^*$$

from the principle of detailed balance [Eq. (4)] and

$$k_{if} \prod_{j=1}^{n_s} u_j^{v'_{ij}} = \exp \left(\ln k_{if} + \sum_{j=1}^{n_s} v'_{ij} \ln u_j \right)$$

for $u_j > 0$. Thus, we deduce by using the mean-value theorem

that

$$\sum_{i=1}^{n_r}(v_{ik}'' - v_{ik}')\left(k_{if}\prod_{j=1}^{n_s}u_j^{v_{ij}'} - k_{ir}\prod_{j=1}^{n_s}u_j^{v_{ij}''}\right) = \sum_{i=1}^{n_r}(v_{ik}'' - v_{ik}')\left[\exp\left(\ln k_{if} + \sum_{j=1}^{n_s}v_{ij}'\ln u_j\right) - \exp\left(\ln k_{ir} + \sum_{j=1}^{n_s}v_{ij}''\ln u_j\right)\right]$$

$$= \sum_{i=1}^{n_r}(v_{ik}'' - v_{ik}')e^{\sigma_i(u)}\left(\ln k_{if} + \sum_{j=1}^{n_s}v_{ij}'\ln u_j - \ln k_{ir} - \sum_{j=1}^{n_s}v_{ij}''\ln u_j\right)$$

$$= \sum_{i=1}^{n_r}e^{\sigma_i(u)}(v_{ik}'' - v_{ik}')\left[\sum_{j=1}^{n_s}(v_{ij}' - v_{ij}'')\ln u_j - \sum_{j=1}^{n_s}(v_{ij}' - v_{ij}'')\ln u_j^*\right]$$

$$= \sum_{i=1}^{n_r}\sum_{j=1}^{n_s}e^{\sigma_i(u)}(v_{ik}'' - v_{ik}')(v_{ij}' - v_{ij}'')(\ln u_j - \ln u_j^*),$$

where $\sigma_i(u)$ is between $(\ln k_{if} + \sum_{j=1}^{n_s}v_{ij}'\ln u_j)$ and $(\ln k_{ir} + \sum_{j=1}^{n_s}v_{ij}''\ln u_j)$. Set

$$S(u) = -\sum_{i=1}^{n_r}e^{\sigma_i(u)}S_i$$

with

$$S_i = [(v_{ik}'' - v_{ik}')(v_{ij}'' - v_{ij}')]$$

a symmetric $n_s \times n_s$ matrix. Obviously, this $S(u)$ is symmetric and nonpositive definite. Moreover, it follows from Eq. (3) that the kinetic Eq. (2) can be rewritten in the form of Eq. (5).

In order to determine the null space of $S(u)$, we recall the elementary fact that the null space of a symmetric and nonpositive definite matrix coincides with the set of vectors at which its quadratic form vanishes. Thus, we compute the quadratic form

$$\xi^T S(u)\xi = -\sum_{i=1}^{n_r}e^{\sigma_i(u)}\xi^T S_i\xi = -\sum_{i=1}^{n_r}e^{\sigma_i(u)}\left|\left(v_{i1}'' - v_{i1}', v_{i2}'' - v_{i2}', \ldots, v_{in_s}'' - v_{in_s}'\right)\xi\right|^2$$

for n_s vector (column) ξ. This quadratic form vanishes if and only if ξ is perpendicular to all $(v_{i1}'' - v_{i1}', v_{i2}'' - v_{i2}', \ldots, v_{in_s}'' - v_{in_s}')^T$ for $i = 1, 2, \ldots, n_r$. Namely, the set of zeros, and thereby the null space of $S(u)$, is

$$\mathrm{span}\left\{\left(v_{i1}'' - v_{i1}', v_{i2}'' - v_{i2}', \ldots, v_{in_s}'' - v_{in_s}'\right)^T, i = 1, 2, \ldots, n_r\right\}^\perp.$$

This completes the proof.

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