

# Entropy production as a universal functional of reaction rate: chemical networks close to steady states

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**Abstract** Entropy production rate (EPR) is the fundamental theoretical quantity in non-equilibrium thermodynamics whereas reaction rate is the primary experimental quantity for a chemical system out-of-equilibrium. In this work, we explore a connection between the above two quantities for general reaction networks. Both cyclic and linear networks of arbitrary dimension are studied, along with a mixed variety. The systems can attain a non-equilibrium steady state (NESS) under chemiostatic condition, which becomes the state of true thermodynamic equilibrium when detailed balance holds. We show that there exists a universal functional relationship of the EPR with reaction rate close to steady states for all the networks considered. Near a NESS, the former varies linearly with the reaction rate. On the other hand, around a true equilibrium, it varies quadratically with the latter. Numerical experiments justify our analytical findings quite transparently.

**Keywords** Entropy production rate · Non-equilibrium steady state · Reaction network

## 1 Introduction

Chemical reaction networks [1–4] have received considerable recent attention on various grounds. These include inhomogeneous catalysis [1], the emergence of positive steady states (SS) [2], bistability [3] etc. Nonlinear networks have also found several applications [4].

Reaction systems have continued to play a primary role in the study of irreversible thermodynamics since inception. In such studies, entropy production rate (EPR) has

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turned out as the most basic and interesting thermodynamic quantity [5–7] to deal with the above chemical systems, both at the time-independent (e.g., SS) and time-dependent situations [8–10]. An SS can be a state of true thermodynamic equilibrium (TE) when the EPR vanishes. In such a case, detailed balance (DB) is obeyed. On the other hand, a constant positive value of the EPR refers to another kind of SS, where DB is not obeyed. This can happen in open systems. One renders concentrations of a few chosen species at constant values by suitable input-output mechanisms, yielding the so-called non-equilibrium steady state (NESS) [11–14]. To state otherwise, such systems involve some reservoirs to act as chemiostats [15, 16], leading to the emergence of SS.

Our purpose here is to explore the behavior of EPR *close* to some SS where the reaction rate is non-zero and the EPR is positive, be the SS a TE or an NESS. However, the EPR is a theoretical measure and, for complex systems, the connection of EPR with the immediately observable quantities may not be apparent. The reaction rate, on the other hand, stands as the primary experimental entity. Therefore, it will be helpful to get a functional relation of the EPR  $\sigma(t)$  with the reaction rate  $v(t)$ . This will be most useful if the functional relation possesses a *universal* character. The present endeavor is aimed at such a goal. Specifically, we show that, close to any SS, EPR can be quite generally expressed in the form  $\sigma(t) = P + Qv(t) + Rv^2(t)$ , where  $P$ ,  $Q$  and  $R$  are constants. Only in case of a TE,  $P = 0 = Q$ . Further, the general forms of  $P$ ,  $Q$  and  $R$  for different types of networks are similar. In other words, the above functional form possesses a sort of universality.

## 2 Formulation

Any complex chemical reaction network contains the part shown in Fig. 1. On the basis of such a scheme, we can write

$$\dot{a}_i = -(k_i + k_{-(i-1)})a_i(t) + k_{i-1}a_{i-1}(t) + k_{-i}a_{i+1}(t), \quad (1)$$

with  $a_i(t)$  being the concentration of species  $A_i$  at time  $t$ .

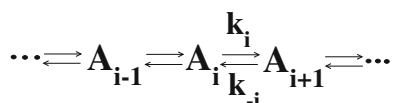
We define the SS as

$$\dot{a}_i = 0, \quad \forall i. \quad (2)$$

Conventionally, the reaction fluxes are defined pairwise, between nearest neighbors. Here we define the flux  $J_i$  as

$$J_i(t) = k_i a_i(t) - k_{-i} a_{i+1}(t). \quad (3)$$

**Fig. 1** Schematic diagram of a part of any complex reaction network indicating the forward and backward rate constants



Accordingly, the thermodynamic force is defined by

$$X_i^{\text{th}} = \mu_i(t) - \mu_{i+1}(t), \quad (4)$$

and the corresponding kinetic one by

$$X_i^{\text{kin}} = T \ln \frac{k_i a_i(t)}{k_{-i} a_{i+1}(t)}. \quad (5)$$

We have set here (and throughout) the Boltzmann constant  $k_B = 1$ . The EPR  $\sigma(t)$  is essentially a product of all fluxes and kinetic forces, leading to

$$\begin{aligned} \sigma(t) &= \frac{1}{T} \sum_i J_i(t) X_i^{\text{kin}} \\ &= \sum_i [k_i a_i(t) - k_{-i} a_{i+1}(t)] \ln \frac{k_i a_i(t)}{k_{-i} a_{i+1}(t)}. \end{aligned} \quad (6)$$

From Eq. (6), it is evident that  $\sigma(t) \geq 0$ . In the long-time limit,  $\sigma$  becomes stationary with a value given by

$$\sigma(\text{SS}) \geq 0. \quad (7)$$

The nature of the SS is characterized by

$$\sigma(\text{TE}) = 0, \quad (8)$$

$$\sigma(\text{NESS}) > 0. \quad (9)$$

We now focus on a situation close to the SS. For that purpose, small deviations in species concentrations from their respective SS values are introduced as

$$\delta_i(t) = a_i(t) - a_i^s. \quad (10)$$

Here  $\{a_i^s\}$  is determined by the set of Eq. (2). Then, using finite difference approximation, one gets for a short time interval  $\tau$

$$\dot{\delta}_i = \dot{a}_i \approx \delta_i / \tau. \quad (11)$$

Now, the reaction rate  $v(t)$  can be suitably defined in terms of the rate of change of concentration of any species  $A_i$  of the reaction network. Thus

$$v(t) = \dot{a}_i. \quad (12)$$

In what follows, we explore whether a general relationship between  $\sigma(t)$  and  $v(t)$  near a SS exists.

### 3 Case studies

A wide variety of reaction networks exists. Particularly important and relevant to chemistry are those that involve tautomeric equilibria and stereoisomerism. Broadly, these networks can be classified as straight-chain or cyclic, with branching allowed in either case. So, studies of a general nature should deal with cases that belong to the above categories. Accordingly, here we apply the formalism by considering the different situations. However, a common feature of all the cases is the presence of two species B and C. Their concentrations are kept fixed at values  $b$  and  $c$ , respectively. Thus, they act as chemiostats. This type of condition can be maintained by continuously injecting B to and removing C from the reaction medium by connecting with reservoirs. The system is thus open and an external drive exists. Therefore, the EPR is positive in all the cases even when  $t \rightarrow \infty$ . Such a mechanism allows the entry of NESS in our discussion. However, when DB holds, the drive vanishes and TE is attained.

#### 3.1 Cyclic network

The scheme of the cyclic network is shown in Fig. 2. The reaction system contains  $N$  number of species whose concentrations vary with time. The kinetic equations are the same as in Eq. (1) with the following periodic boundary conditions:

$$\begin{aligned} i - 1 = N, & \text{ for } i = 1, \\ i + 1 = 1, & \text{ for } i = N. \end{aligned}$$

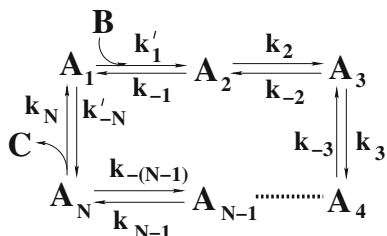
Here we have set  $k_1 = k'_1 b$  and  $k_{-N} = k'_{-N} c$ . So the forward rate constant  $k_1$  of reaction  $i = 1$  and the reverse rate constant  $k_{-N}$  of reaction  $i = N$  are pseudo-first-order rate constants. The net reaction flux of the  $i$ -th reaction is already defined in Eq. (3). The expression of EPR for the reaction system shown in Fig. 2 is given by

$$\sigma_C(t) = \sum_{i=1}^N J_i(t) \ln \frac{k_i a_i(t)}{k_{-i} a_{i+1}(t)}. \tag{13}$$

Using Eqs. (10) and (11) in Eq. (1), we get

$$(1 - (k_i + k_{-(i-1)})\tau) \delta_i(t) + k_{i-1} \tau \delta_{i-1}(t) + k_{-i} \tau \delta_{i+1}(t) = 0. \tag{14}$$

**Fig. 2** Schematic diagram of the cyclic reaction network indicating the forward and backward rate constants of each reaction. Species B and C act as chemiostats



As the reactions are coupled, so the  $\delta_i$ s are related to each other and can be expressed in terms of any one of them, say  $\delta_1$ . Then, one can write

$$\delta_i = f_i \delta_1, \quad \text{with } f_1 = 1. \quad (15)$$

In the next paragraph, we will discuss how to determine the  $f_i$ s.

The set of coupled Eq. (14), with the help of Eq. (15), can be cast in the matrix form

$$\mathbf{M}\mathbf{f} = \mathbf{0}. \quad (16)$$

Here  $\mathbf{f}$  is a  $N \times 1$  matrix with  $\mathbf{f}^T = (f_1, f_2, \dots, f_N)$  and  $\mathbf{M}$  is a  $N \times N$  matrix with the property

$$\begin{aligned} M_{ij} &\neq 0, \text{ for } j = i, i-1, i+1 \\ M_{ij} &= 0, \text{ otherwise.} \end{aligned} \quad (17)$$

The non-zero matrix elements are

$$M_{ii} = (1 - (k_i + k_{-(i-1)})\tau), \quad (18)$$

$$M_{i,i-1} = k_{i-1}\tau, \quad (19)$$

$$M_{i,i+1} = k_{-i}\tau. \quad (20)$$

From Eqs. (16) and (17), we obtain a recursion relation

$$f_j = -\frac{(M_{j-1,j-2}f_{j-2} + M_{j-1,j-1}f_{j-1})}{M_{j-1,j}}, \quad j = 2, 3, \dots, N, \quad (21)$$

with the boundary conditions:

$$f_0 = f_N, \quad M_{j,0} = M_{j,N}.$$

The first of the relations becomes

$$f_2 = -\frac{M_{1N}f_N + M_{11}}{M_{12}}. \quad (22)$$

Then, it is easy to follow from Eq. (21) that, all the other  $f_j$ s can be expressed in terms of  $f_N$ . Now, from the condition

$$\sum_{i=1}^N a_i = \text{constant}, \quad (23)$$

we get

$$\sum_{i=1}^N \delta_i = 0, \quad (24)$$

and using Eq. (15), we have

$$\sum_{i=2}^N f_i = -1. \tag{25}$$

From Eqs. (18)–(22) and (25), one can determine the  $f_i$ s in Eq. (15).

With the above relations, we now explore the EPR near the NESS. From Eq. (1), we have

$$J_i^s = J, \quad (i = 1, \dots, N) \tag{26}$$

at NESS. Then, from Eqs. (10), (13), (15) and (26) and using the smallness of  $\delta_i$ s, the EPR near NESS becomes

$$\begin{aligned} \sigma_C(t) &= \sum_{i=1}^N (J + k_i \delta_i - k_{-i} \delta_{i+1}) \left( \ln \frac{k_i a_i^s}{k_{-i} a_{i+1}^s} + \frac{\delta_i}{a_i^s} - \frac{\delta_{i+1}}{a_{i+1}^s} \right) \\ &= X_1 + Y_1 \delta_1 + Z_1 \delta_1^2, \end{aligned} \tag{27}$$

with

$$X_1 = J \ln \frac{\prod_{i=1}^N k_i}{\prod_{i=1}^N k_{-i}}, \tag{28}$$

$$Y_1 = \sum_{i=1}^N (k_i f_i - k_{-i} f_{i+1}) \ln \frac{k_i a_i^s}{k_{-i} a_{i+1}^s}, \tag{29}$$

$$Z_1 = \sum_{i=1}^N (k_i f_i - k_{-i} f_{i+1}) \left( \frac{f_i}{a_i^s} - \frac{f_{i+1}}{a_{i+1}^s} \right). \tag{30}$$

We take the reaction rate as  $v(t) = a_1$  here and throughout. This is due to the fact that, all the deviations in concentration from the NESS are defined in terms of  $\delta_1$ . Then, from Eq. (1) with  $i = 1$  and using Eq. (15) along with the periodic boundary conditions, we get near NESS

$$v(t) = R_1 \delta_1, \tag{31}$$

where

$$R_1 = -(k_1 + k_{-N}) + k_N f_N + k_{-1} f_2. \tag{32}$$

Hence, from Eqs. (27) and (31), near NESS we can express the EPR as

$$\sigma_C(t) = P_C + Q_C v(t) + R_C v^2(t), \tag{33}$$

where  $P_C = X_1$ ,  $Q_C = Y_1/R_1$  and  $R_C = Z_1/R_1^2$ .

If the cyclic reaction network reaches TE, then from the ratios of equilibrium concentrations of the species, we have

$$\frac{a_2^e a_3^e \dots a_N^e a_1^e}{a_1^e a_2^e \dots a_{N-1}^e a_N^e} = 1 = \frac{\prod_{i=1}^N k_i}{\prod_{i=1}^N k_{-i}}. \quad (34)$$

This is the constraint on the rate constants in order to satisfy DB. Equation (34) implies  $X_1 = 0$ . When DB holds, the fluxes in Eq. (3) vanish and this leads to  $Y_1 = 0$ . Then near the TE, EPR reduces to

$$\sigma_C(t) = R_C v^2(t). \quad (35)$$

In this case,  $R_C$  contains equilibrium concentrations. Evaluation of the quantities  $P_C$ ,  $Q_C$ ,  $R_C$  requires full description of the reaction kinetics which is a formidable task. Still, from Eq. (35), we can gain a semi-quantitative understanding of EPR near TE from the reaction velocity data.

### 3.2 Linear network

The scheme of the linear network is shown in Fig. 3. Like the cyclic network, the system contains  $N$  number of species whose concentrations are time-dependent.

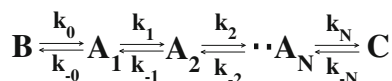
The only difference is that here the chemiostats B and C are connected only with  $A_1$  and  $A_N$ , respectively. Therefore, there are  $N + 1$  reactions with the reaction flux defined as

$$J_i(t) = k_i a_i(t) - k_{-i} a_{i+1}(t), \quad i = 0, 1, \dots, N, \quad (36)$$

with  $a_0 = b$  and  $a_{N+1} = c$  being time-independent. At NESS, Eq. (26) holds for the linear network, with  $i = 0, 1, \dots, N$ . The rate equations of the reaction system are also identical to those given in Eq. (1). Defining small deviations around NESS as in Eq. (10), one gets similar set of coupled equations given in Eq. (14). For the linear network, however, the boundary conditions are changed to

$$\delta_0 = 0 = \delta_{N+1}$$

as B and C are chemiostats. Applying Eq. (15) to the linear network, it follows easily that the recursion relation for the cyclic network given in Eq. (21) is equally valid for the linear network with



**Fig. 3** Schematic diagram of the linear reaction network indicating the forward and backward rate constants. Species B and C act as chemiostats

$$f_0 = 0 = f_{N+1}.$$

Therefore, the expression of EPR for the linear network close to NESS becomes

$$\begin{aligned} \sigma_L(t) &= \sum_{i=0}^N (J + k_i \delta_i - k_{-i} \delta_{i+1}) \left( \ln \frac{k_i a_i^s}{k_{-i} a_{i+1}^s} + \frac{\delta_i}{a_i^s} - \frac{\delta_{i+1}}{a_{i+1}^s} \right) \\ &= X_2 + Y_2 \delta_1 + Z_2 \delta_1^2, \end{aligned} \tag{37}$$

where

$$X_2 = J \ln \frac{a_0 \prod_{i=0}^N k_i}{a_{N+1} \prod_{i=0}^N k_{-i}}, \tag{38}$$

$$Y_2 = \sum_{i=0}^N (k_i f_i - k_{-i} f_{i+1}) \ln \frac{k_i a_i^s}{k_{-i} a_{i+1}^s}, \tag{39}$$

$$Z_2 = \sum_{i=0}^N (k_i f_i - k_{-i} f_{i+1}) \left( \frac{f_i}{a_i^s} - \frac{f_{i+1}}{a_{i+1}^s} \right). \tag{40}$$

Let us now define the reaction velocity of the linear network as  $v(t) = a_i$  as in the cyclic network. Then using Eq. (15) in Eq. (1) with  $i = 1$ , one obtains near NESS

$$v(t) = R_2 \delta_1, \tag{41}$$

with

$$R_2 = -(k_1 + k_{-0}) + k_{-1} f_2. \tag{42}$$

Then, from Eqs. (37) and (41), the EPR for the linear network near NESS can be written as

$$\sigma_L(t) = P_L + Q_L v(t) + R_L v^2(t), \tag{43}$$

with  $P_L = X_2$ ,  $Q_L = Y_2/R_2$  and  $R_L = Z_2/R_2^2$ .

Now we consider the case of TE. At TE we can write

$$\frac{a_1^e a_2^e a_3^e \dots a_N^e a_{N+1}}{a_0 a_1^e a_2^e a_{N-1}^e a_N^e} = \frac{\prod_{i=0}^N k_i}{\prod_{i=0}^N k_{-i}}, \tag{44}$$

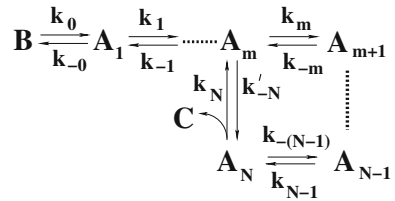
that leads to

$$\frac{a_0 \prod_{i=0}^N k_i}{a_{N+1} \prod_{i=0}^N k_{-i}} = 1 \tag{45}$$

and hence,  $X_2 = 0$ . Satisfaction of the DB also means  $Y_2 = 0$ . So, the EPR near TE becomes



**Fig. 4** Schematic diagram of the mixed reaction network indicating the forward and backward rate constants. Species B and C act as chemistats



$$\sigma_L(t) = R_L v^2(t). \quad (46)$$

We clarify that,  $R_L$  in Eq. (46) is defined in terms of equilibrium concentrations.

### 3.3 Mixed network

We consider now a reaction network which is composed of cyclic and linear parts. The kinetic scheme is depicted in Fig. 4. Again, the species  $A_i$  ( $i = 1, \dots, N$ ) have time-varying concentrations  $a_i(t)$ . According to the scheme in Fig. 4, the kinetic equations of the system are written as

$$\dot{a}_i = -(k_i + k_{-(i-1)} + k_{-N}\delta_{im})a_i(t) + k_{i-1}a_{i-1}(t) + k_{-i}a_{i+1}(t) + k_N a_N \delta_{im} \quad (47)$$

where  $\delta_{jk}$  stands for the Kronecker delta symbol. The boundary conditions are:  $a_0 = b$ ,  $a_{N+1} = a_m$ . Here the pseudo-first-order rate constant is defined as  $k_{-N} = k'_{-N}c$ .

For the mixed network, the equivalent of Eq. (14) is given by

$$\begin{aligned} (1 - (k_i + k_{-(i-1)} + k_{-N}\delta_{im})\tau) \delta_i(t) + k_{i-1}\tau \delta_{i-1}(t) \\ + k_{-i}\tau \delta_{i+1}(t) + k_N\tau \delta_N \delta_{im} = 0. \end{aligned} \quad (48)$$

Using Eq. (15), the set of Eq. (48) can be expressed in a matrix form similar to Eq. (16). The properties of the matrix  $\mathbf{M}$  are now given as

$$\begin{aligned} M_{ij} &\neq 0, \text{ for } j = i, i - 1, i + 1 \\ M_{ij} &\neq 0, \text{ for } i = m, j = N \\ M_{ij} &= 0, \text{ otherwise.} \end{aligned} \quad (49)$$

The non-zero matrix elements are

$$M_{ii} = (1 - (k_i + k_{-(i-1)} + k_{-N}\delta_{im})\tau), \quad (50)$$

$$M_{i,i-1} = k_{i-1}\tau, \quad (51)$$

$$M_{i,i+1} = k_{-i}\tau. \quad (52)$$

$$M_{m,N} = k_N\tau. \quad (53)$$

Then, one obtains a recursion relation, similar in structure to Eq. (21), as

$$f_j = -\frac{(M_{j-1,j-2}f_{j-2} + M_{j-1,j-1}f_{j-1} + M_{j-1,N}f_N\delta_{j-1,m})}{M_{j-1,j}}, \quad j = 2, \dots, N, \tag{54}$$

with the boundary conditions:

$$f_0 = M_{j,0} = 0.$$

with  $f_1 = 1$ , all the  $f_j$ s can be determined following similar procedure as discussed for the cyclic network.

At SS, it follows from Eq. (47) that

$$\begin{aligned} J_i^s &= 0, \text{ for } i = 0, \dots, m - 1 \\ J_i^s &= J, \text{ for } i = m, m + 1, \dots, N. \end{aligned} \tag{55}$$

This is an important *difference* between the mixed network and the previous ones for which Eq. (26) is valid. The expression of the EPR near NESS then becomes

$$\begin{aligned} \sigma_M(t) &= \sum_{i=0}^N (J_i^s + k_i\delta_i - k_{-i}\delta_{i+1}) \left( \ln \frac{k_i a_i^s}{k_{-i} a_{i+1}^s} + \frac{\delta_i}{a_i^s} - \frac{\delta_{i+1}}{a_{i+1}^s} \right) \\ &= X_3 + Y_3\delta_1 + Z_3\delta_1^2, \end{aligned} \tag{56}$$

where

$$X_3 = J \ln \frac{\prod_{i=m}^N k_i}{\prod_{i=m}^N k_{-i}}, \tag{57}$$

$$Y_3 = \sum_{i=0}^N (k_i f_i - k_{-i} f_{i+1}) \ln \frac{k_i a_i^s}{k_{-i} a_{i+1}^s}, \tag{58}$$

$$Z_3 = \sum_{i=0}^N (k_i f_i - k_{-i} f_{i+1}) \left( \frac{f_i}{a_i^s} - \frac{f_{i+1}}{a_{i+1}^s} \right). \tag{59}$$

Defining the reaction rate  $v(t) = a_1$  as in the previous cases, we obtain

$$v(t) = R_2\delta_1 \tag{60}$$

near NESS, with  $R_2$  given in Eq. (42). Then, from Eqs. (56) and (60), near NESS the EPR for the mixed network can be written as

$$\sigma_M(t) = P_M + Q_M v(t) + R_M v^2(t). \tag{61}$$

Here  $P_M = X_3$ ,  $Q_M = Y_3/R_2$  and  $R_M = Z_3/R_2^2$ .

At TE, DB holds in the form

$$\frac{\prod_{i=m}^N k_i}{\prod_{i=m}^N k_{-i}} = 1 \quad (62)$$

and all the fluxes vanish implying  $J = 0$ . This gives  $X_3 = 0 = Y_3$ . Then, from Eq. (61) we have

$$\sigma_M(t) = R_M v^2(t). \quad (63)$$

Again,  $R_M$  in Eq. (63) contains equilibrium concentrations.

## 4 Results and discussion

In this section, we numerically verify the analytical results given in Eqs. (33), (43) and (61). We choose a mixed network shown in Fig. 5 containing four species  $A_i$  ( $i = 1, \dots, 4$ ) with time-dependent concentrations  $a_i(t)$ . This network can be generated from the general scheme of Fig. 4 with  $N = 4$  and  $m = 2$ . The rate constants are taken as:  $k_1 = 0.2$ ,  $k_2 = 0.1$ ,  $k_3 = 0.2$ ,  $k_4 = 0.3$ ,  $k_{-1} = 0.1$ ,  $k_{-2} = 0.3$ ,  $k_{-3} = 0.1$ , all in  $s^{-1}$ . Following Eq. (62), DB is satisfied in this case for

$$\frac{k_2 k_3 k_4}{k_{-2} k_{-3} k_{-4}} = 1.$$

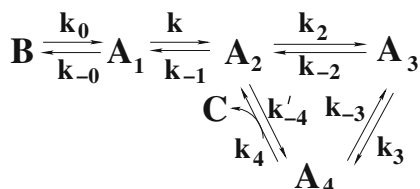
Thus, we set  $k_{-4} = k'_{-4}[C] = 0.2$  for system reaching TE. Any other value of  $k_{-4}$  will lead the system to NESS. Here we set  $k_{-4} = 1.5$  for that purpose. We define the reaction rate as

$$v(t) = \dot{a}_3.$$

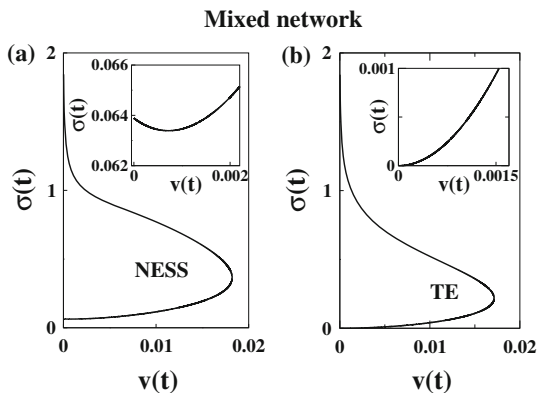
Such a choice of reaction rate is convenient to allow a smooth passage from the scheme of mixed network in Fig. 5 to a purely cyclic or a purely linear network by setting some of the rate constants equal to zero. In this process, only the rate equation of  $a_3$  remains unchanged. As may be seen, the results derived in Eqs. (33), (43) and (61) do not depend on the choice of reaction rate.

We show the variation of  $\sigma(t)$  as a function of  $v(t)$  in Fig. 6 for the network under consideration. In all cases that follow, the EPR is determined numerically using the

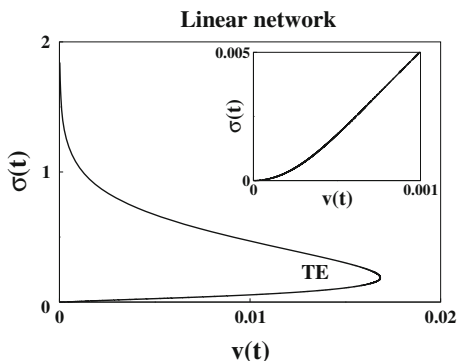
**Fig. 5** Schematic diagram of the mixed reaction network containing four species  $A_i$  ( $i = 1, \dots, 4$ ) with time-dependent concentrations  $a_i(t)$ . Species B and C act as chemistats



**Fig. 6** Variation of  $\sigma(t)$  as a function of reaction rate  $v(t)$  for the mixed network shown in Fig. 5 for the reaction system reaching **a** NESS and **b** TE. The insets depict the behavior of  $\sigma(t)$  near SS in respective cases



**Fig. 7** Variation of  $\sigma(t)$  as a function of reaction rate  $v(t)$  for the linear network, obtained from the scheme in Fig. 5 with  $k_4 = 0 = k_{-4}$ . The inset depicts the behavior of  $\sigma(t)$  near TE

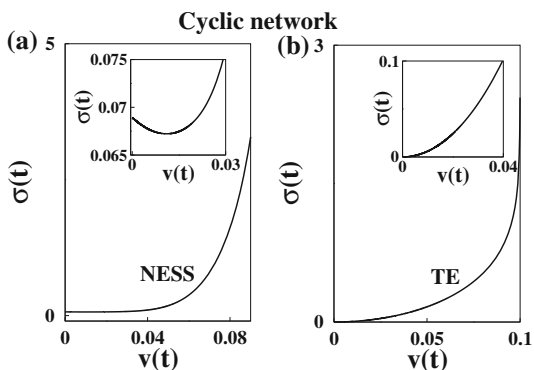


form given in Eq. (6). The case of NESS (Fig. 6a) involves a non-zero value of  $\sigma(t)$  at  $v = 0$  whereas, at TE (Fig. 6b)  $\sigma(t) = 0$ . These features are clearly seen in the figure. At low  $v(t)$ , it is also evident from the inset of Fig. 6a that, at first  $\sigma(t)$  decreases linearly with  $v(t)$ , followed by a quadratic rise, confirming Eq. (61). The inset in Fig. 6b, on the other hand, shows that  $\sigma(t)$  varies quadratically with  $v(t)$  near TE. This behavior follows from Eq. (63).

We now set  $k_4 = 0 = k_{-4}$  to generate a linear network. The concentration [B] is kept constant at an arbitrary value. However, a comparison with Fig. 3 shows that there is no scope of NESS now because of the absence of any reservoir at the other extreme. Therefore, the system can only reach TE with  $\sigma = 0$ . The near-equilibrium situation is nevertheless characterized by a quadratic rise of  $\sigma(t)$  with  $v(t)$ , in tune with the prediction of Eq. (46). Figure 7 bears testimony to these two features.

Finally, we construct a purely cyclic network from Fig. 5 by choosing  $k_0 = k_{-0} = k_1 = k_{-1} = 0$ . In this case, one can imagine a sink D to exist between  $A_2$  and  $A_3$  in such a way that  $A_2$  converts itself to  $A_3 + D$ . One then finds in the cycle both a source and a sink to sustain an NESS. As a special case, the DB can also be recovered. The outcomes are displayed in Fig. 8 where we again notice a non-zero  $\sigma$  when  $t \rightarrow \infty$  along with a linear decay with  $v(t)$  as  $v(t) \rightarrow 0$  (Fig. 8a). As usual, however, the TE is characterized by  $\sigma = 0$  at  $v = 0$  and a quadratic rise for small  $v(t)$ .

**Fig. 8** Variation of  $\sigma(t)$  as a function of reaction rate  $v(t)$  for the purely cyclic network, obtained from the scheme in Fig. 5 with  $k_0 = k_{-0} = k_1 = k_{-1} = 0$ . The reaction system can reach **a** an NESS and obviously, **b** TE. The insets depict the behavior of  $\sigma(t)$  near SS in respective cases



## 5 Summary

In summary, we notice that the expressions of  $\sigma_C$  in Eq. (33),  $\sigma_L$  in Eq. (43) and  $\sigma_M$  in Eq. (61) have the same structure in the small  $v(t)$  regime. This has the general form  $\sigma_J(t) = P_J + Q_J v(t) + R_J v^2(t)$ , ( $J \equiv C, L, M$ ), where  $P_J$ ,  $Q_J$  and  $R_J$  are constants. For the special case of a TE, we also found that  $P_J = 0 = Q_J$ , implying a quadratic growth with  $v(t)$  as  $v(t) \rightarrow 0$ . The coefficients  $P_J$ ,  $Q_J$  and  $R_J$  possess similar forms as well. Therefore, on the basis of comparison of the expressions for  $\sigma(t)$  in all the reaction networks studied, we may conclude that there exists a universal functional relationship of the former with reaction rate close to any SS. These results should act as steps towards the final goal of connecting the key theoretical construct like EPR with real-life data.

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